

ELECTRON PARAMAGNETIC RESONANCE OF  $\text{Mn}^{2+}$   
AND  $\text{VO}^{2+}$  IN SINGLE CRYSTALS

A Thesis Submitted

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by

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to the

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This is to certify that the work presented  
in this thesis has been performed by Mr. A. V.  
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## PREFACE

Electron spin resonance offers a wide variety of applications. The symmetry of crystalline field influences the resonance spectrum in a predetermined fashion and as such resonance phenomena can supplement x-ray diffraction techniques. In suitable cases a small percentage of metal ions can be replaced by any suitable paramagnetic ion and the paramagnetic resonance spectrum of the ion will enable the position of the metal ion in the structure to be determined to an accuracy of about  $1^\circ$  to  $3^\circ$ . Similarly the bond direction of a molecular ion consisting of a paramagnetic metal and oxygen atoms with reference to the direction of metal-oxygen bond in the crystal can be determined by studying the resonance spectrum. Changes in phase which are temperature dependent can be detected more readily as compared to x-ray and dielectric measurements and the transition temperature can be determined to an accuracy of about  $1^\circ\text{C}$ . In addition, some information as to the sites becoming magnetically inequivalent can be obtained automatically. The defects occurring in the crystalline solids, the position and the behaviour of vacancies formed therein can be studied with the help of a resonance spectrum. The degree of covalency can also be determined with its help.

Figs. (3.2), (3.3) and (3.4) show the three spectra related to the  $z$ ,  $y$  and  $x$  axes respectively of the complex.

Angular variation studies and spin-Hamiltonian analysis of these spectra lead to the identification of the complex. In this complex  $Mn^{2+}$  is found to substitute a  $\beta$ - $Cs^+$  position and get associated in the ab-plane with the nearest neighbour  $\beta$ - $Cs^+$  vacancy, the direction of association being the  $z$ -axis of the complex. The  $y$ -axis of this complex is in the same ab plane at an angle of  $90^\circ$  to the  $z$ -axis while its  $x$ -axis is along the  $c$ -axis of the crystal and is perpendicular to the plane containing  $y$  and  $z$  axes of the complex.

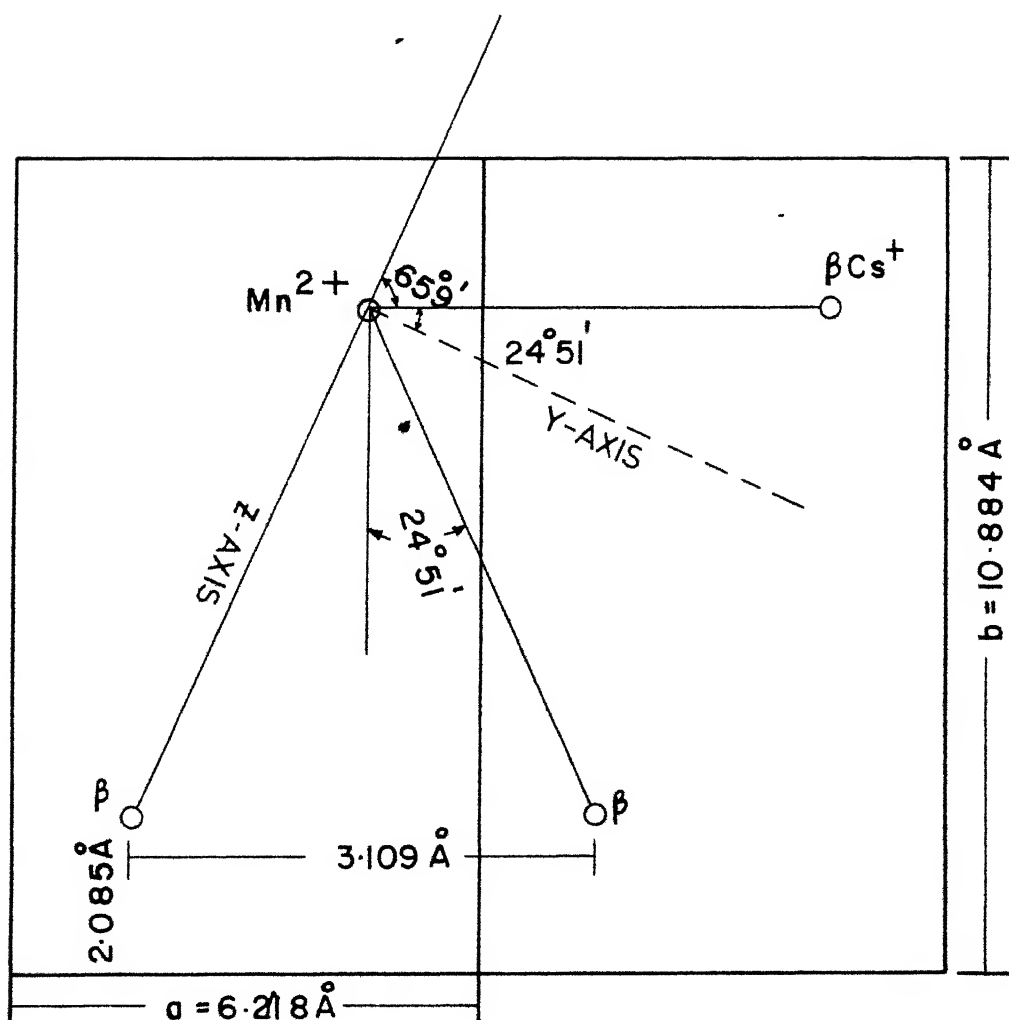
The angle which this complex is expected to make with a known direction in the crystal, say,  $b$ -axis, is calculated from the structural parameters as obtained from x-ray studies<sup>9</sup>; this agrees fairly well with that obtained from resonance data. Fig.(3.5) gives the proposed model for the observed vacancy complex. For this complex which is in the  $ab$ -plane the  $z$ -axis makes an angle of  $25^\circ$  with the crystallographic  $b$ -axis the calculated angle being  $24^\circ 51'$ . The associated vacancy can occur in any one of the directions  $Mn^{2+} - \beta Cs^+$  (Fig.3.5) and one expects two identical spectra when the static magnetic field is making equal angles of  $24^\circ 51'$  each on either side of b axis.

In this thesis the author has used the phenomenon of spin resonance to study these varied aspects in some detail. All spectra have been recorded for the first time except two of the vacancy spectra in  $\text{Mn}^{2+}$ -doped sodium fluoride.

Chapter I is divided into two parts. Part one serves as an introduction to the phenomenon of Electron Paramagnetic Resonance, (EPR). In part two is described the work reported in this thesis broadly.

Chapter II gives the necessary theoretical background in interpreting EPR spectra reported in this thesis. Crystal field parameters necessary to describe crystalline fields of lower symmetry and the energy levels one expects when the spin of anion influences the paramagnetic ion are discussed in detail for transition metal ions in general with particular reference to the ions studied.

Chapter III describes the EPR spectrum of divalent manganese ion in single crystals of caesium sulphate at 9.5 Gc/sec. It has been found that in the ab- plane the divalent manganese ion  $\text{Mn}^{2+}$  takes the place of a monovalent site of caesium ion  $\text{Cs}^+$ . The line joining  $\text{Mn}^{2+}$  ion and the associated vacancy at  $\text{Cs}^+$  site makes an angle of  $25^\circ$  with the crystallographic b-axis in the ab-plane. Correlation with the known x-ray diffraction



3.5. MODEL OF  $\beta\beta$ -COMPLEX IN THE  $ab$  PLANE OF  $\text{Cs}_2\text{SO}_4:\text{Mn}^{2+}$  CRYSTAL -  $\text{Mn}^{2+}$  SUBSTITUTED IN THE  $\beta$ - $\text{Cs}^+$  POSITION AND THE NEAREST NEIGHBOUR  $\beta$ 's ARE THE ASSOCIATED VACANCIES.

TABLE 3.6

The Lines of  $\text{Mn}^{2+}:\text{Cs}_2\text{SO}_4$  at Room Temperature 20 °C  
 $H \parallel x$ -axis of the complex  
 (All values in Oersted)

DPPH<sup>a</sup> 3376

Line	$-3/2 \leftrightarrow -5/2$	$-1/2 \leftrightarrow -3/2$	$-1/2$	$\leftrightarrow +1/2$	$1/2$	$\leftrightarrow +3/2$	$+5/2 \leftrightarrow +3/2$
	Ob- serv- ed	cal- culat- ed	Ob- serv- ed	cal- culat- ed	Ob- serv- ed	cal- culat- ed	Ob- serv- ed
1844	1821	2192	2207	2724	3383	3411	5020
1927	1902	2283	2290	2814	3486	3499	5098
2009	1985	2361	2376	2903	3571	3590	5184
2098	2071	2449	2465	3002	3667	3684	5284
2192	2160	2537	2556	3096	3758	3780	5389
2283	2251	2630	2649	3192	3837	3879	5496
							5484

Standard deviation 19; <sup>a</sup>Diphenylpicrylhydrazyl

Input parameters (for second order perturbation equations 3.2(a)):

$$A_x(-B)=-91; A_z(=A)=-93; A_y(=C)=-91$$

$$H_{ox}=3357 (g_x=2.0149); D_x=452; E_x=475; (b_4^0)_x=-8; (b_4^2)_x=-45$$

studies on crystal structure indicate that the ions responsible are  $\beta$ -Cs<sup>+</sup> ions. This complex gives rise to three spectra which have been analysed using an electron spin  $S=5/2$  and nuclear spin  $I=5/2$  in the orthorhombic spin Hamiltonian. The values of the crystal field parameters are refined by diagonalising the relevant  $36 \times 36$  energy matrix. In this chapter are also included temperature variation studies from room temperature to liquid nitrogen temperature. Throughout this temperature range the nature of the spectrum does not change and the crystalline field parameters varied smoothly indicating there is no detectable phase transition in this temperature range.

While the position of metal ion studies in caesium sulphate are described in chapter III, in chapter IV are described the spin resonance spectra of  $\text{VO}^{2+}$  molecular ion under the influence of highly asymmetric crystalline field of caesium sulphate. The spectrum obtained is somewhat complicated. A tentative analysis of the spectrum suggests that the  $\text{VO}^{2+}$  ion probably substitutes the  $\alpha$ -Cs<sup>+</sup> ions. The V-O bond appears to have three preferential directions: one along the c-axis of the crystal, one in a direction making an angle of  $30^\circ$  with the c-axis in the bc plane and yet another nearly along the a-axis. These directions are the directions of nearest approach from the position of  $\alpha$ -Cs<sup>+</sup> to the neighbouring oxygens. The possibility of the existence



#### 4.1 INTRODUCTION

The electron paramagnetic resonance (EPR) of  $\text{VO}^{2+}$  in single crystals of alkali halides<sup>1</sup>,  $\text{NH}_4\text{Cl}$ <sup>2</sup> and  $\text{KNO}_3$  and  $\text{CsNO}_3$ <sup>3</sup> is known to be independent of the orientation of the crystal with respect to the magnetic field direction indicating that there is no preferred orientation of the V-O bond axis in these crystals. On the other hand, it is strongly angular dependent in crystals of Tutton salts<sup>4</sup> and alkali alums<sup>5,6,7</sup> doped with  $\text{VO}^{2+}$  showing the existence of preferred orientation of V-O bond. The EPR studies on  $\text{Mn}^{2+}$  ion in caesium sulphate have given interesting information about the associated lattice defects. The present work on caesium sulphate doped with  $\text{VO}^{2+}$  ion has been taken up to get information about the structure of vanadyl complex in the crystal and also about the associated lattice defects.

#### 4.2 THEORY

A tetravalent vanadium ion with outer electronic configuration  $3d^1$  exists in the most stable form as  $\text{VO}^{2+}$  the binding with the oxygen being highly covalent. The LCAO-MO description of this molecular ion in the complex  $\text{VO}(\text{H}_2\text{O})_5^{2+}$  had shown<sup>8,9</sup> that the unpaired "d" electron occupies a non-bonding  $b_2$  type vanadium orbital ( $3d_{xy}$ ) the lowest state thus being an orbital singlet. Due to the magnetic interaction with the vanadium nucleus

of canted axes is investigated by a harmonic analysis of  $g^2-\theta$  curves studied in the three principal crystallographic planes. The  $g^2$ -matrix has been obtained from the appropriate second order equations by the method of least squares and it is diagonalised to give the three principal  $g$ -values and nine direction cosines of the principal axes of the  $g$ -tensor with reference to the known crystallographic axes. The crystallographic axes themselves are identified from an analysis of x-ray rotation photographs.

In chapter V the EPR spectrum of divalent manganese in sodium fluoride has been presented. In addition to the determination of the parameters in the ... spectra found by other workers, a new isotropic spectrum consisting of six lines and a broad line resonance have been found and analysed. Superhyperfine structure, SHFS, due to surrounding fluorine ions has been analysed in all spectra. Determination of SHFS parameters in the isotropic spectrum and in the spectrum designated 'weak' by earlier workers is new to this work. A number of weak lines at very low fields have been observed which are due to half-field transitions. Temperature variation studies have been made from 300 °C down to liquid nitrogen temperature and a vacancy model has been proposed.



In chapter VI electron spin resonance studies of vanadyl molecular ion in single crystals of sodium, potassium and rubidium chloride have been described in a temperature range 77 °K to 330 °K. At liquid nitrogen temperature anisotropic spectra are recorded in each case while at room temperature only isotropic spectra are observed suggesting there is a fast readjustment of  $\text{VO}^{2+}$  molecular ion in these crystals at high temperatures while this tumbling motion has been hindered at very low temperatures. Spin-Hamiltonian constants are calculated from isotropic and anisotropic spectra recorded in each case. The line widths in each case are found to obey a law originally put forward by Kivelson. The haphazard orientation of  $\text{VO}^{2+}$  bond in these alkali chloride crystals which do not contain oxygen is in contrast with oriented VO-bond studies described in chapter IV in the case of vanadyl-doped caesium sulphate. They are explained on the assumption that the medium behaves as a liquid for  $\text{VO}^{2+}$  molecular ion as far as the paramagnetic resonance behaviour is concerned.

be a highly distorted coordination with practically all the metal ion oxygen distances being different from one another (Fig. 4.1a). It is, however, very easy to visualise a  $C_{\infty v}$  local symmetry for the  $VO^{2+}$  ion in all the three complexes discussed in this chapter. Though the present experiments cannot unambiguously describe the type of coordination involved, the optical absorption studies and the EPR studies definitely show the formation and existence of the  $VO^{2+}$  ion in the  $Cs_2SO_4$  crystal.

It is interesting and in a way puzzling to note that while the present work indicates that  $VO^{2+}$  substitutes  $-Cs^+$  ions in  $Cs_2SO_4$  crystal, the work of Pande<sup>20</sup> in our laboratory shows that  $VO^{2+}$  substitutes  $\beta-NH_4^+$  ions in  $(NH_4)_2SO_4$  single crystal. However, such type of differences in substitution have been found earlier in the  $(NH_4)_2SO_4$  and alkali sulphate crystals.  $Mn^{2+}$  is found<sup>21</sup> to substitute one of the two possible types ( $\alpha$  or  $\beta$ ) of  $NH_4^+$  ions in  $(NH_4)_2SO_4$  and get associated with the second type of  $NH_4^+$  vacancy. On the other hand in  $K_2SO_4$ <sup>22</sup> and  $Cs_2SO_4$  (chapter III) crystals,  $Mn^{2+}$  substitutes  $\beta-K^+$  (or  $Cs^+$ ) ion and gets associated with a  $\beta$ -alkali ion vacancy.

It is to be pointed out that there are a number of unmarked lines in the Figures 4.2 — 4.6. It is possible that they are due to some additional complexes of  $VO^{2+}$  which are as yet unidentified.

These chapters are followed by appendices giving up-to-date information on g-values of the ions studied in various lattices and computer programs used in the calculation. The diagonalisation program is a standard one using Jacobi's method adopted for the particular needs of the problem while the least square programs in other cases are especially written. A bibliography of the work done on manganese and vanadyl ions in various lattices is included here.

If the crystalline field has a higher symmetry, say, cubic,  $D=0$  and it splits  ${}^6S_{5/2}$  into a doublet and a quartet. In moderate crystalline fields, the zero field splittings will be so small that the fine structure cannot be resolved, and the spectrum contains only isotropic sextet at  $g = 2$ .

#### 5.4 RESULTS AND DISCUSSION

Four different kinds of spectra have been observed and are designated as spectra I, II, III<sub>2</sub> and III<sub>4</sub> for a convenient comparison with the corresponding spectra<sup>6</sup> in  $Mn^{2+}; NaCl$ . The spectrum I represents a broad overlapping absorption which is more prominent at low temperature. This is due to  $Mn^{2+}$  ions which occur in aggregates or clusters. Spectrum II shows a hyperfine sextet and is due to  $Mn^{2+}$  ions at the alkali sites having a cubic site symmetry with no nearby alkali vacancies. Spectra III<sub>2</sub> and III<sub>4</sub> are due to  $Mn^{2+}$  ions at the alkali sites with tetragonal site symmetries, the  $\langle 100 \rangle$  axis being the tetragonal axis. These two spectra have been observed and analyzed by the earlier workers though no specific models have been proposed. Hall et al<sup>13</sup> identified these spectra as due to  $Mn^{2+}$  ions associated with vacancies. Spectrum III<sub>2</sub> has a large spread compared to spectrum III<sub>4</sub> showing that the  $Mn^{2+}$  ions responsible for spectrum III<sub>2</sub> experience a larger crystalline field compared to those responsible for spectrum III<sub>4</sub>. These observations indicate that the complex responsible for the spectrum III<sub>2</sub> is a  $Mn^{2+}$  ion

CHAPTER I  
INTRODUCTION



## 1.1 Electron Paramagnetic Resonance .

The seeds of magnetic resonance phenomena were laid in 1936 when Gorter<sup>1</sup> demonstrated that a paramagnetic salt placed in a high frequency alternating magnetic field absorbed energy and that this was influenced by the application of a static magnetic field either parallel or perpendicular to the alternating magnetic field. The development of electronics during the second Historical world war placed high frequency oscillators at the disposal of experimentalists. Zaviosky<sup>2</sup> in Russia and Cumberrow and Halliday<sup>3</sup> in U.S.A obtained the first paramagnetic resonance absorption spectra. Since then the phenomena of paramagnetic resonance has become quite useful in fundamental research.

The principle of the method is as follows. Consider a paramagnetic ion. It has a magnetic moment and therefore its ground state is degenerate. If this ion is placed in a strong static magnetic field the degeneracy is lifted and the energy levels undergo a Zeeman Principle splitting. Application of an oscillating magnetic field of appropriate frequency will be able to induce transitions between the Zeeman levels and energy is absorbed from the electromagnetic field. If the static magnetic field is slowly varied the absorption shows a series of maxima. The plot between the absorbed energy and the magnetic field is called the electron paramagnetic resonance spectrum or electron

The corresponding spectra are shown in Figs.(5.2),(5.3) and (5.4) respectively in which the calculated SHFS patterns are also drawn to scale. The values obtained for the constants  $A_g$  and  $A_\sigma$  for all the three spectra are given in Table (5.4) where the data available from the earlier work on spectrum III<sub>4</sub> are also included.

Watkins<sup>5</sup> has shown that the halogen ion nearer to the charge compensating vacancy undergoes a slight displacement towards the divalent impurity ion. The effect of such a displacement of F<sup>-</sup> ions is not detected in the present SHFS and also in the study of Mn<sup>2+</sup>:KF<sup>17</sup>.

spin resonance spectrum. The phenomenon itself is called electron paramagnetic resonance, EPR, or electron spin resonance, ESR.

A system of charges exhibits paramagnetism whenever it has a resultant angular momentum. Among the paramagnetic substances may be mentioned the transition Paramagnetic species group of elements containing 3d, 4f and 5f electrons, monoatomic gases such as atomic hydrogen with its ground state  $^2S_{1/2}$ , oxygen gas with the molecule in the ground state  $^3\Sigma_g^-$ , or organic free radicals such as diphenylpicrylhydrazyl, (DPPH), having an unpaired electron. Fig. 1.1 shows the structure of DPPH which is often used for calibration in EPR spectra. If a substance is not paramagnetic, it can be exposed to high energy radiation<sup>4</sup> or subjected to mechanical stresses<sup>5</sup> so that the normal bonds are disrupted and paramagnetic species are formed.

All the work reported in this thesis was conducted at x-band with spectrometer operating at nearly  $0.3 \text{ cm}^{-1}$ . Fig. 1.2 shows the block diagram of the essentials of the equipment.

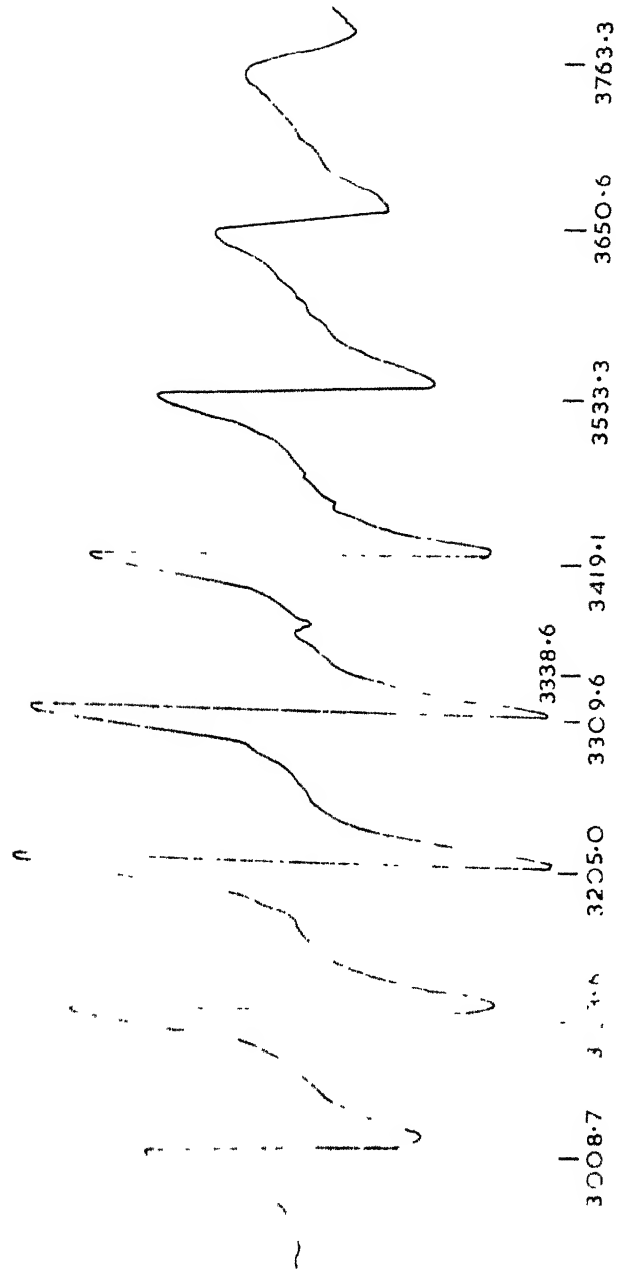
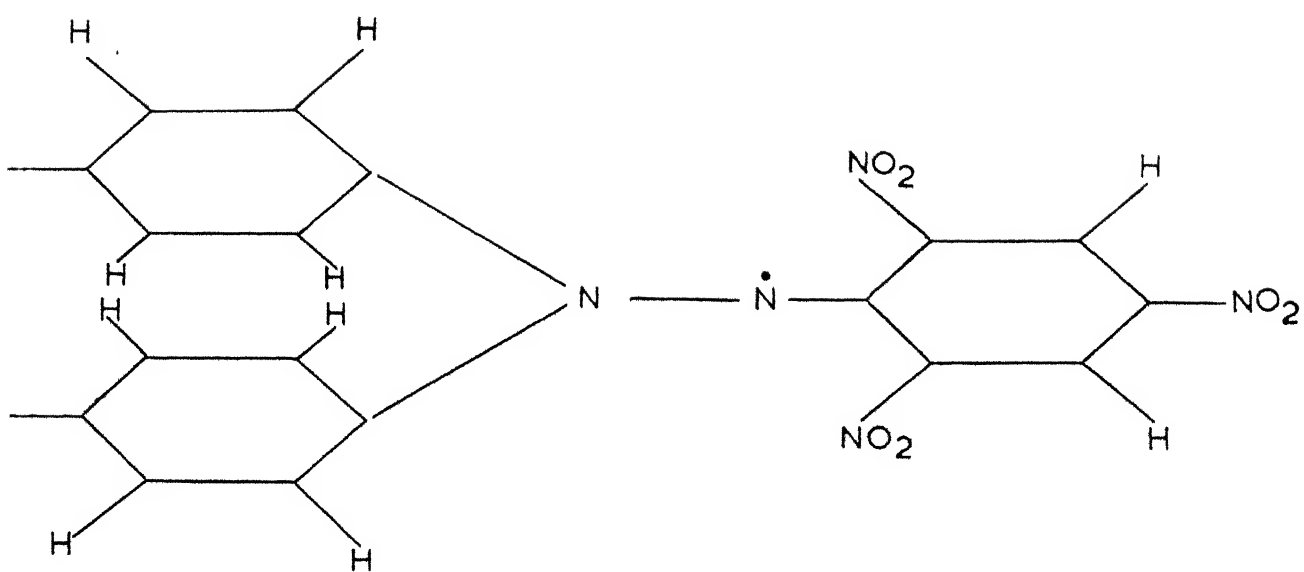


FIG-6.1 SPECTRUM I ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF  $\text{VO}_2^+$  IN NQCl AT ROOM TEMPERATURE. THE X-COORDINATE REPRESENTS MAGNETIC FIELD VALUES IN GAUSS.



MOLECULAR STRUCTURE OF D.P.P.H

THE DOT OVER N SHOWS THE UNPAIRED ELECTRON THE MAGNETIC  
 FIELD WHICH INTERACTS WITH EITHER OF THE NITROGEN NUCLEI

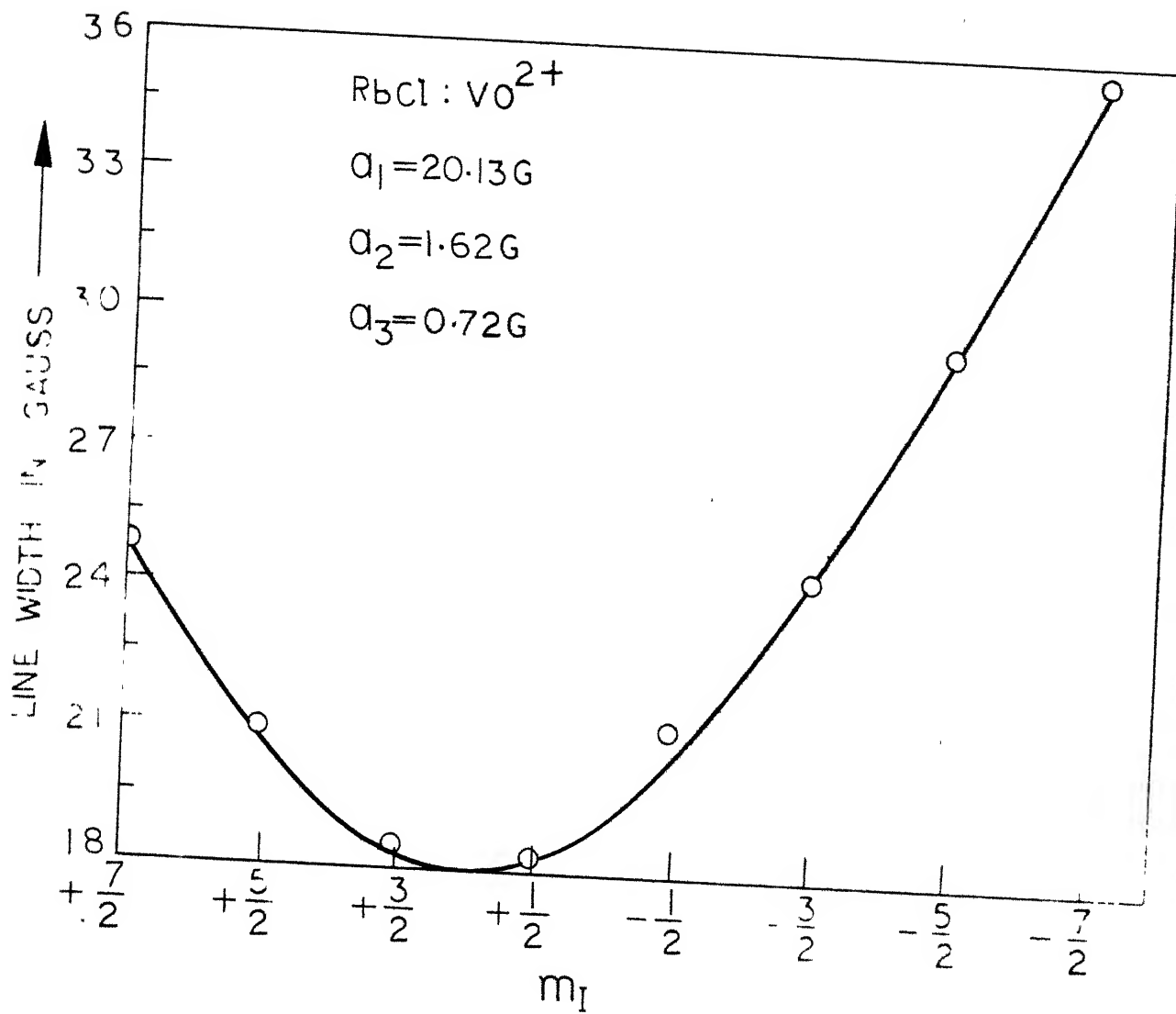


FIG. 5. PLOT OF LINE WIDTH VERSUS  $m_I$  IN THE CASE OF  $\text{RbCl:VO}^{2+}$  SYSTEM. THE SOLID CURVE REPRESENTS PREDICTED VARIATION OF THE LINE WIDTH WHILE CIRCLES INDICATE ACTUAL EXPERIMENTAL VALUES AT ROOM TEMPERATURE.

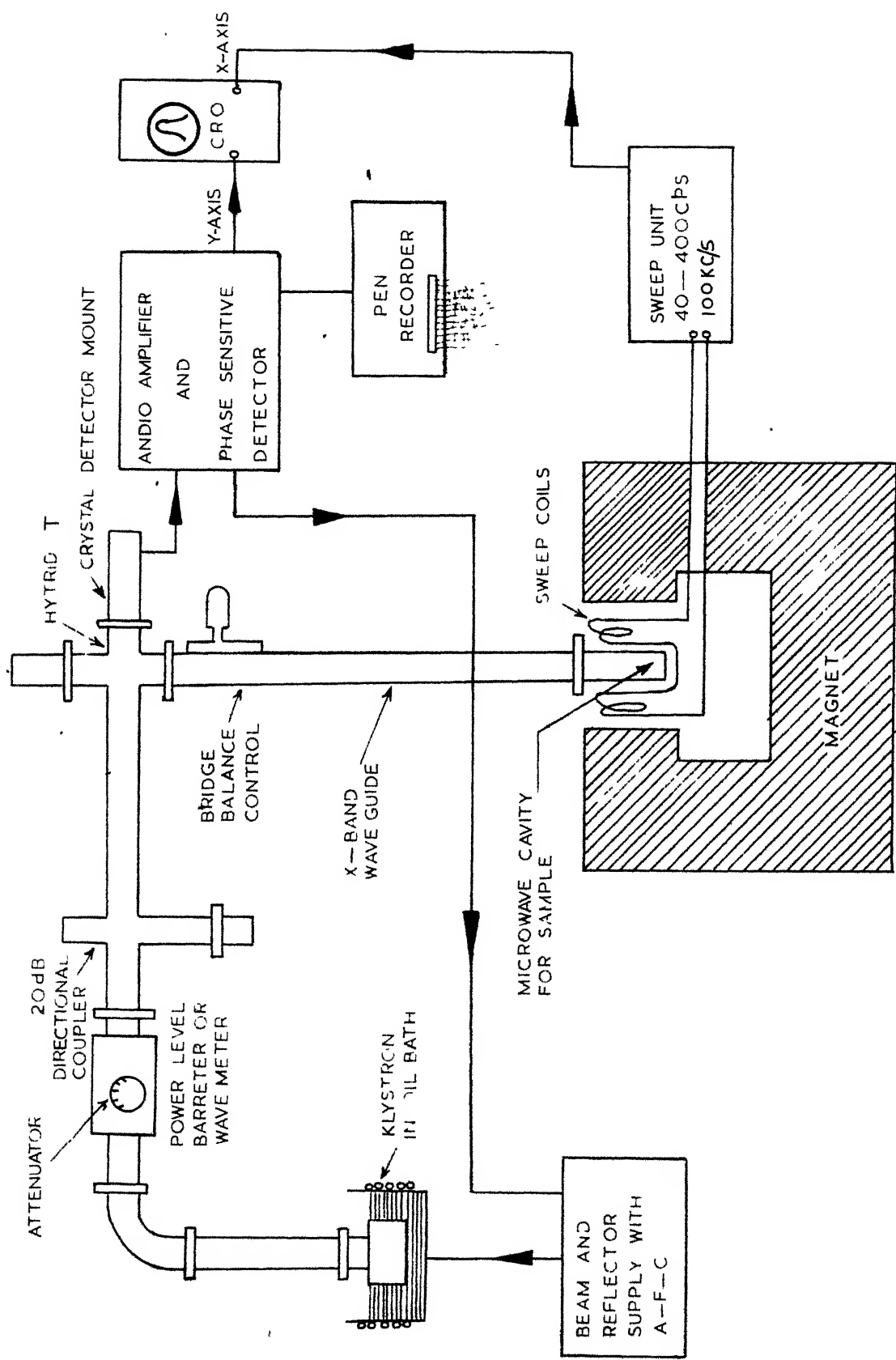


FIG12 BLOCK DIAGRAM OF X-BAND EPR SPECTROMETER (VARIAN MODEL)

- (p) Work was done at x-band  
 Room temperature parameters 300 °K  
 Error in g's 0.003; error in D is 7 Oe;  
 error in E is 3 Oe; error in A's 1 Oe  
 $b_4^0 = 0 \pm 1$  Oe;  $b_4^2 = 13$  Oe ;  $b_4^4 = -77$  Oe

The complex is in the ab plane;  $Mn^{2+}$  ion substitutes  
 $-Cs^+$  ion and gets associated itself with a vacancy  
 at a nearest neighbour  $-Cs^+$  site.  
 The angle between the direction of the complex taken  
 as z axis and the crystallographic c-axis is  $25 \pm 1^\circ$ .

- (q) Work was done at x-band  
 Room temperature parameters 300 °K  
 Error in g's 0.0001; error in A's 0.5 Oe  
 Three orientations of V-O bond giving rise to three  
 complexes have been reported.  
 Complex I is in the direction of crystallographic c-  
 axis  
 Complex II makes an angle of  $30^\circ$  to the c-axis in  
 the bc plane  
 Complex III is nearly along the crystallographic  
 a-axis.



Let us consider a system of ions in a magnetic field  $H_0$ . Assuming the ion obeys Russel-Saunders or LS-coupling, the situation would be that the total orbital magnetic moment  $L$  and the total spin moment  $S$  combine to give a resultant  $J$ . This precesses round the field with a frequency  $2\pi\nu_0$ . Corresponding to  $M_J$  values,  $J \geq M_J \geq -J$ , there will be  $2J+1$  energy levels which are equally spaced.

$$E_{M_J} = g_0 \beta H_0 M_J \quad \dots (1.1)$$

Application of a periodic magnetic field  $H \cos 2\pi\nu t$  perpendicular to the direction of static magnetic field  $H_0$  results in magnetic dipole transitions between adjacent levels such that  $\Delta M = \pm 1$ . When the resonance condition is satisfied one has  $\nu = \nu_0$  and

$$\begin{array}{l} \text{The resonance} \\ \text{condition} \end{array} \quad E_M - E_{M'} = g_0 \beta H_0 = h\nu \quad \dots (1.2)$$

This is the quantum mechanical picture of resonance; the corresponding classical frequency is  $\nu$ .

The quantity  $g$  in equation (1.2) is called the 'spectroscopic splitting factor'<sup>6</sup> as this determines the magnitude of the splitting of energy levels in a magnetic field. This is an important quantity which is obtained even in those cases where the resonance spectrum consists of even a single line. For a free ion the value of  $g$  is very nearly 2. Fidone and Stevens<sup>7</sup> pointed out that the effects of

## VITAE

A.V.Jagannadham was born on 15th February, 1924 in Gudivada Agraharam, Andhra Pradesh. He received his Education from the Secondary to Degree stage at Maharajah's College, Vizianagram. After taking B.Sc degree with Physics Main and Mathematics and Chemistry as subsidiary subjects from Andhra University in 1944 he studied at Benares Hindu University and took his M.Sc degree in Physics in 1946. Since then he was teaching Physics to Degree and Post-graduate students at Birla College, Pilani (affiliated to the Agra University), Government College, Ajmer (Affiliated to the University of Rajasthan) and Trichandra College, Nepal, Kathmandu (Affiliated to the Tribhuwan University). He took his early training in x-ray crystallography under Prof. K. Banerji in Allahabad University, Allahabad and Indian Association for the Cultivation of Science, Calcutta. He is on Study Leave from the Government of Rajasthan since July 1964 and is a graduate student in the Physics Department of the Indian Institute of Technology, Kanpur.

covalent bonding can give positive contribution to  $g$  while the departure from the free ion value of 2.002322 in either direction gives an idea of the effective covalent bonding when the ion is subjected to a crystalline field<sup>7,8</sup>. In crystals the value of  $g$  may vary with the direction of the applied field. This anisotropy in  $g$ -value is related to spin-orbit coupling which mixes the ground state of the free ion with the excited states. Thus the electronic moment gets a definite contribution from the otherwise quenched orbital angular momentum.

When once the resonance condition is achieved there are other factors which control the continuous absorption of energy of the electromagnetic field by the spin system. At any temperature and frequency, the lower state is more populated than the upper one. To make this population difference significant the paramagnetic substance is cooled to liquid nitrogen or liquid helium temperatures and higher frequencies are employed. With the absorption of microwave power the population difference tends to equalise itself and unless there is a mechanism which establishes the population difference continuously, paramagnetic resonance absorption ceases to be significant. Such mechanisms are called relaxation processes. The lattice itself plays an important role in this respect. It acts like a huge reservoir with which the spin system exchanges energy.

The rate of this process is characterised by the spin-lattice relaxation time and is intimately related to the line width of the paramagnetic resonance spectrum.

Microwave electronics play a large part in proper detection of the EPR signal. The paramagnetic sample is placed in a cavity resonator in the region of maximum radio frequency magnetic field. The form of microwave magnetic field as existing in a typical rectangular cavity operating in  $TE_{012}$  mode is shown in Fig. 1.3<sup>9</sup>. The effect on losses and resulting frequency shifts in the microwave cavity follow the general equation for electrically resonant systems<sup>10</sup>. The changes in quantities involved are detected using an impedance bridge.(Fig.1.2).

The power absorbed by a paramagnetic specimen in a resonant cavity is proportional to the static magnetic susceptibility  $\chi_0$ . In the dynamic phenomena it is usual to consider susceptibility as a complex quantity:  $\chi = \chi' - i\chi''$ . Here  $\chi'$  is the dynamic susceptibility and represents the magnetisation which changes in phase with the field while  $\chi''$  determines the absorption of energy from the periodic magnetic field. The general relation between these two quantities is given by Kramers-Kronig equations<sup>11</sup>.

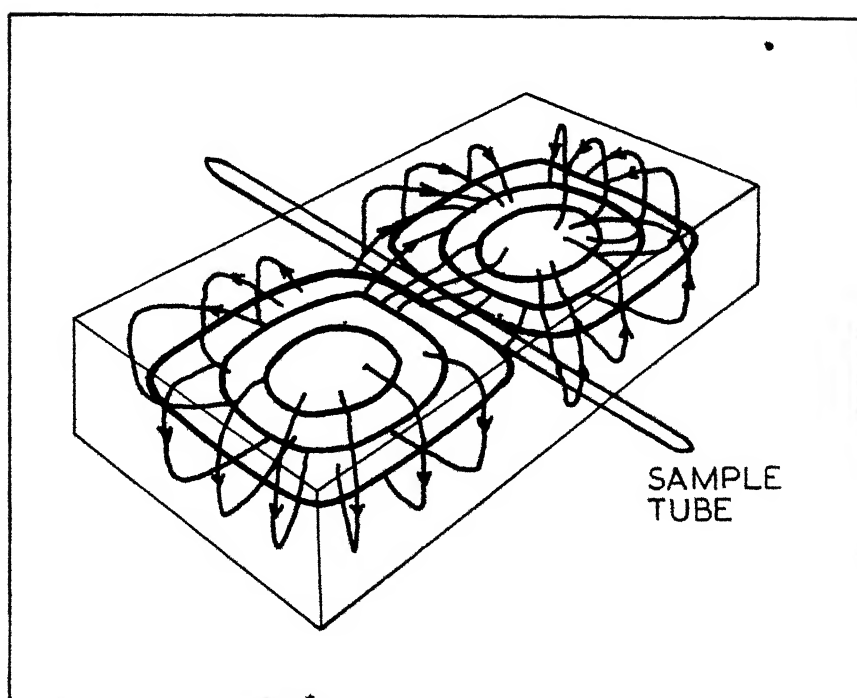


FIG-13 MICROWAVE MAGNETIC FIELDS IN  $TE_{012}$  MODE

An oscillating magnetic field can be thought of as a superposition of two rotating magnetic fields. Any precessing magnetic moment induced by a rotating magnetic

Paramagnetic dispersion and absorption	field can be described in terms of frequency sensitive susceptibility. The susceptibility is maximum at resonance.
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At resonance the Kramers-Kronig relations insure that the radio frequency susceptibility is a complex quantity and there will be both dispersion and energy dissipation from the rotating field. Fig. 1.4<sup>12</sup> shows the form of curves of paramagnetic resonance absorption and dispersion of susceptibility as the field is varied.

EPR would be of academic interest only if the magnetic states of the electron were independent of its surroundings. But it so happens that the interaction between the electron and its surroundings perturb the magnetic states of the system giving rise to additional transitions. This means EPR can be used with advantage and serves as a powerful tool in various applications in solid state physics. Low and Offenbacher<sup>13</sup> reviewed the

Scope of EPR	success of paramagnetic resonance as an important structural tool in perovskites, spinels, and garnets as it often determines the site preference of a particular magnetic ion, the point symmetry, distortion of cubic symmetry and the number of inequivalent magnetic sites so that it has been possible to find the 'single ion' contribution to the magnetic anisotropy.
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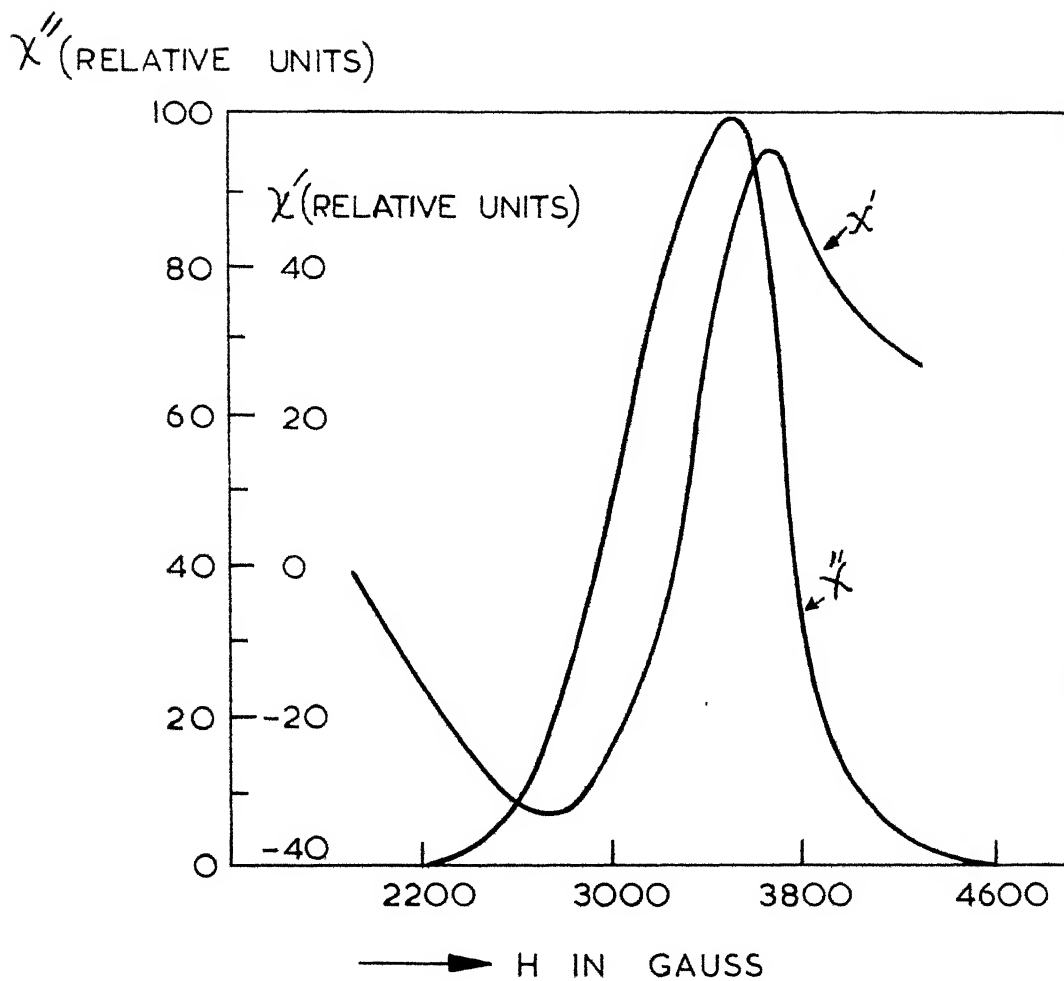


FIG.4 PARAMAGNETIC RESONANCE ABSORPTION ( $\chi''$ ) AND DISPERSION ( $\chi'$ ) OF SUSCEPTIBILITY VERSUS MAGNETIC FIELD (TYPICAL VARIATION) AT X-BAND.

A survey of the Physical and Solid State applications is given by Ingram<sup>14</sup>. Bennet and Blackmore<sup>15</sup> recently used electron spin resonance spectroscopy to determine the absolute concentrations of hydrogen atoms in a gas-flow system at room temperature at total pressures between one and ten torr.

## 1.2 Present Investigation

In this thesis  $\text{Mn}^{2+}$  and  $\text{VO}^{2+}$  are studied after doping any one of them in minute concentrations in single crystals of caesium sulphate ( $\text{Cs}_2\text{SO}_4$ ), sodium fluoride ( $\text{NaF}$ ) and chlorides of sodium, potassium and rubidium. The object of these studies is three-fold. It is proposed to utilise the EPR techniques firstly to determine the site preference of the doubly charged  $\text{Mn}^{2+}$  magnetic ion doped in alkali sulphates. In the general study of doped alkali sulphates which has been taken in our laboratory a few years ago<sup>16,17</sup>, caesium sulphate ( $\text{Cs}_2\text{SO}_4$ ) doped with divalent manganese in concentrations of the order of three hundred parts per million has been taken for complete analysis. The site preference of  $\text{Mn}^{2+}$  ion to various  $\text{Cs}^+$  ions is studied and the magnetic axial directions are correlated with the positions of  $\text{Cs}^+$  ions as known from x-ray studies. Spin-Hamiltonian parameters of various magnetic complexes are determined first by using second order perturbation theory to the spectra obtained in three mutually perpendicular directions. Later the parameters so obtained



have been refined by using the fine structure and the hyperfine structure matrix for the ion placed in a field of rhombic symmetry and determining the eigenvalues by diagonalising it. The parameters have been varied slightly to reproduce the observed eigenvalues by a least square fit. Temperature variation studies of these parameters in the range 300 °K to 77 °K indicated that there is no detectable phase transformation in the case of  $\text{Cs}_2\text{SO}_4$  single crystal doped with  $\text{Mn}^{2+}$  in this temperature interval.

The vanadyl ion is also doped in the single crystals of caesium sulphate to investigate the direction of VO bond in these crystals. Whereas  $\text{Mn}^{2+}$  entered the host lattice substitutionally in the  $\text{Cs}^+$  positions, the charge compensation occurring due to the formation of vacancies in appropriate positions,  $\text{VO}^{2+}$  enters substitutionally at a  $\text{Cs}^+$  position in giving highly angular dependent spectra. The variation of g-tensor and A-tensor has been investigated in the three planes and the direction cosines of these tensors and their principal values have been determined by forming the appropriate matrix and diagonalising it. These studies form an attempt to investigate the relative VO direction with respective oxygens in the sulphate group in this crystal by using a magnetic probe of a vanadyl complex. All the spectra obtained by doping divalent manganese ion and molecular vanadyl ion in caesium sulphate have been analysed for the first time.

The second type of studies are undertaken to estimate the effects of ligands of the host lattice of the doped ion. For this purpose EPR spectra of divalent manganese doped in single crystal of sodium fluoride (NaF) are studied in a temperature range of 573 °K to 77 °K. A complicated spectrum of more than 540 lines has been analysed. Three distinct complexes have been isolated one of which has been analysed for the first time. The interaction of d-electron of the doped manganese with the fluorine ligands of the host gave an extensive superhyperfine structure which has been analysed completely in all spectra. High temperature studies have been done and a model for the doped crystal has been suggested.

The third type of studies concern with the line widths of EPR spectra. For this purpose the vanadyl ion has been chosen. This molecular ion has been doped in oxygen-free host lattices of sodium, potassium and rubidium chlorides. Unlike the studies of  $\text{VO}^{2+}$  doped caesium sulphate single crystals, the EPR of vanadyl ion in these host lattices is interesting in that the ion enters the lattices without forming oriented magnetic complexes. Such studies are important in two ways: firstly, the EPR spectrum can be used for a rapid quantitative determination of the vanadium present in the matrix and this has important economic bearing in oil and glass technology; secondly, the relaxation processes in solids can be studied. In this thesis EPR studies of vanadyl ion doped in single crystals

of sodium chloride, potassium chloride and rubidium chloride are described and the line widths are found to have an  $m_I$  dependence as originally suggested by Kivelson<sup>18</sup> who developed a theory of line widths in liquids. Temperature variation studies have indicated that at very low temperatures there is a very fast readjustment of vanadyl ion and the 'Brownian tumbling motion'<sup>19</sup> is partly arrested. This purely temperature effect has been detected in the anisotropic spectrum which is obtained at liquid nitrogen temperature.

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## CHAPTER II

## THEORY AND INTERPRETATION OF EPR SPECTRA

ABSTRACT        The general theory of EPR of transition metal ions and complexes is outlined with a special reference to the spectra of the ions  $V^{4+}$  and  $Mn^{2+}$ . The energy levels of the d-electrons in crystalline fields of various symmetries are briefly described. Basic features of the spin Hamiltonian formalism as a guide to interpreting EPR spectra are mentioned. The g-tensor in ions with  $S=\frac{1}{2}$  has been described. General features concerning hyperfine splitting from the metal nucleus, covalent bonding and ligand hyperfine structure are also discussed. Theory of EPR spectra in liquids with a special reference to vanadyl molecular ion is given.

## 2.1 Introduction

The unpaired d-electrons in the ions of iron group transition metals render them paramagnetic. Table 2.1 gives the number of electrons, spin-orbit constant, spin arrangement of free ion and the total spin in the case of tetravalent vanadium and divalent manganese.

TABLE 2.1

Characteristics of some free ions of  
the Iron-group Transition Metals

Ions	Con- figu- ra- tion	Spin- orbit cons- tant $\lambda$ in $\text{cm}^{-1}$	Spin ar- range- ment of free ion	Total spin $S$	Ground state	Nuclear spin $I$ and abundance
$\text{V}^{4+}$	3 $d^1$	154	$\uparrow$ ---	$\frac{1}{2}$	$^2D_{3/2}$	$7/2(\text{V}^{51})99.8\%$
$\text{Mn}^{2+}$	3 $d^5$	347	$\uparrow\uparrow\uparrow\uparrow$	$5/2$	$^6S_{5/2}$	$5/2(\text{Mn}^{55})100\%$

## 2.2 The d-orbitals of a free-ion:

For a d-electron the  $\ell$ -value is 2 and the total orbital degeneracy is 5. The degeneracy is partly lifted when the d electron is placed in a crystalline field of octahedral or tetrahedral symmetry. The three-fold degenerate orbitals are designated as  $t$  and the two-fold degenerate ones as  $e$ .

$$\begin{aligned}
 & \begin{array}{c} \text{t} \rightarrow \end{array} \begin{array}{c} \text{---} \end{array} \\
 & d_{xy} = \frac{1}{\sqrt{2}} (\phi_{22} - \phi_{2-2}) \\
 & \quad = R_{3d}(r) \cdot \frac{\sqrt{15}}{2} \cdot \sqrt{11} xy \\
 & d_{xz} = \frac{1}{\sqrt{2}} (\phi_{21} + \phi_{2-1}) \quad \dots (2.1) \\
 & \quad = R_{3d}(r) \cdot \frac{\sqrt{15}}{2} \cdot \sqrt{11} xz \\
 & d_{yz} = \frac{1}{\sqrt{2}} (\phi_{21} - \phi_{2-1}) \\
 & \quad = R_{3d}(r) \cdot \frac{\sqrt{15}}{2} \cdot \sqrt{11} yz
 \end{aligned}$$

$$\begin{aligned}
 & \begin{array}{c} \text{e} \rightarrow \end{array} \begin{array}{c} \text{---} \end{array} \\
 & d_{x^2-y^2} = \frac{1}{\sqrt{2}} (\phi_{22} + \phi_{2-2}) \\
 & \quad = R_{3d}(r) \cdot \frac{\sqrt{15}}{4} \cdot \sqrt{11} (x^2 - y^2) \quad \dots (2.2) \\
 & d_{z^2} = \phi_{20} \\
 & \quad = R_{3d}(r) \cdot \frac{\sqrt{15}}{4} \cdot \sqrt{11} (2z^2 - x^2 - y^2)
 \end{aligned}$$

where  $x, y$  and  $z$  are taken as the coordinates of a point at unit distance from the origin,  $R_{3d}(r)$  is the radial wave function for a  $3d$  electron; and the  $\phi_{22}$  et cetera are the  $\phi_{l m_l}$ . These are illustrated graphically in Fig2.1 When the crystal field symmetry is lower than cubic the orbital degeneracy of both  $t$  and  $e$  orbitals could be further partly or completely lifted.

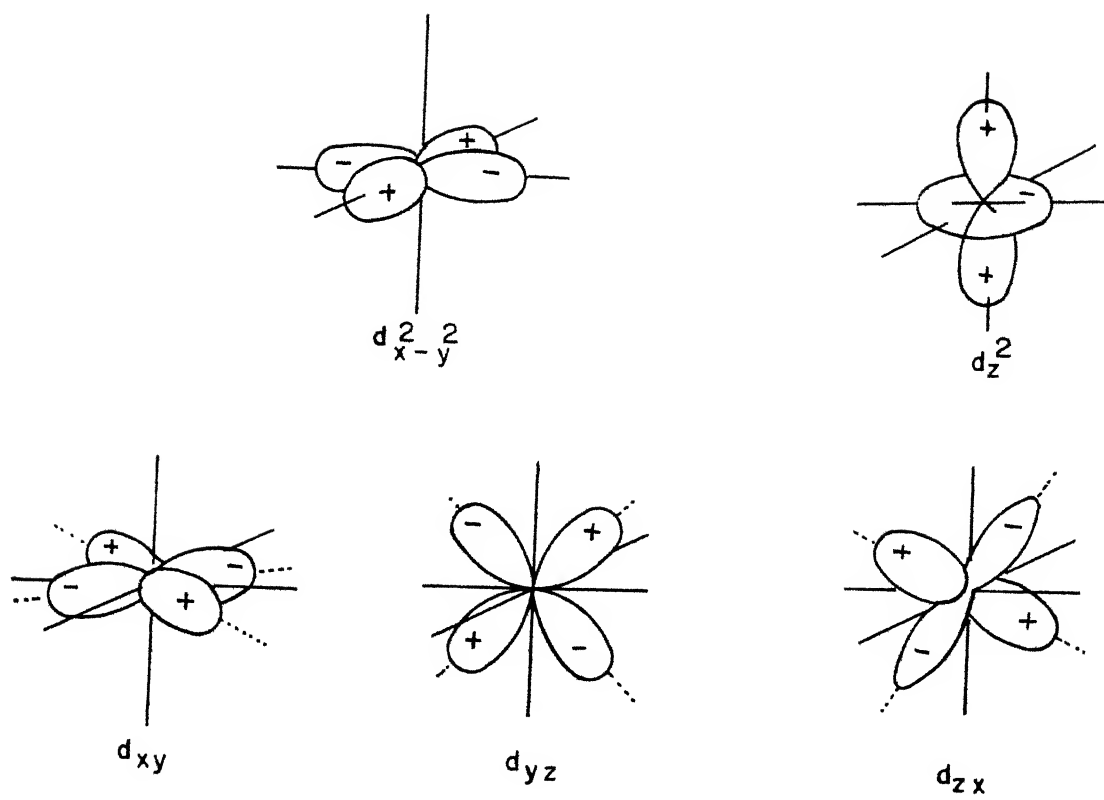


FIG. 2.1 REAL FORMS OF THE  $d$ -ORBITALS



### 2.3 Effect of ligand field on energy levels

If a paramagnetic ion such as  $\text{Mn}^{2+}$  is placed substitutionally at a cation site in a crystal of NaF or  $\text{Cs}_2\text{SO}_4$ , it is surrounded by  $\text{F}^-$  ions or  $\text{SO}_4^{2-}$  ions respectively. These are called "ligands". The number of ligands surrounding the central ion is called the coordination number. These ligands which may be negative ions or neutral molecules with a permanent lone pair of electrons change the energy level scheme with the result we have "ligand-field splitting" of the d-orbitals of the embedded paramagnetic ion. Usually, the orbital degeneracy of the d-orbitals is partly or fully removed by the crystal field. In NaF the  $\text{F}^-$  ligands form nearly octahedral coordination about the  $\text{Mn}^{2+}$  ion. The electrostatic field of the negative charges and the covalent bonding with the ligand orbitals affect the d-electrons of the metal ion. This causes the energy levels corresponding to  $d_{z^2}$  and  $d_{x^2-y^2}$  to be raised and those corresponding to  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  to be lowered. The energy gap between these two types of orbitals is the ligand-field splitting and is called  $\Delta$  or  $10Dq$  by convention.<sup>1</sup> Fig.(2.2)b shows the energy level scheme for this type of symmetry.

The ligands often cause distortion of the atomic orbitals of the paramagnetic ion so that very few complexes in the solid state actually possess regular symmetry. Thus the classification of regular symmetries

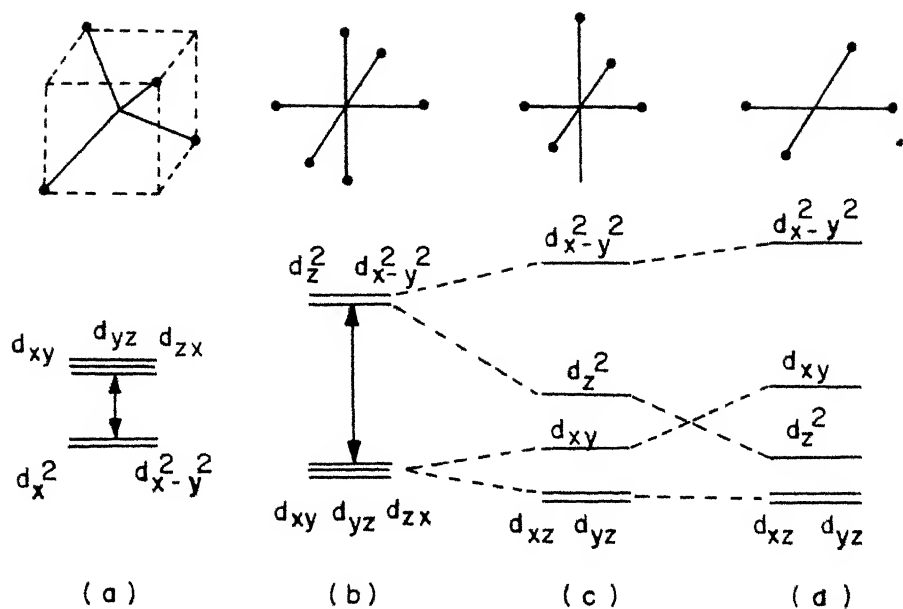


FIG.2.2 SPLITTING OF THE  $d$ -ORBITALS UNDER THE INFLUENCE OF LIGANDS WITH DIFFERENT SYMMETRY

- (a) TETRAHEDRAL
- (b) OCTAHEDRAL
- (c) OCTAHEDRON WITH TETRAGONAL DISTORTION
- (d) SQUARE PLANAR

referred to in Fig.(2.2) are only ideal. Table(2.2) gives the notation and transformation properties of atomic orbitals under crystalline fields of different symmetries. Paramagnetic resonance experiments reveal easily tetragonal or trigonal distortions in cubic systems. The tetragonal distortion in tetrahedral complexes corresponds to a flattening of the tetrahedron, Fig. 2.3(a), while the trigonal distortion in octohedral complexes correspond to a slight compression or elongation along a three-fold axis, Fig. 2.3(c). The effect of these distortions is a further removal of degeneracy of d-orbitals, Fig. 2.3(b), (d). However, the splitting of energy levels in the absence of a magnetic field is governed by Kramers' Theorem: in a system containing an odd number of electrons, at least twofold degeneracy must remain in the absence of a magnetic field. The pairs of states, (Kramers' doublets"), involved are time-conjugate, one being obtained from the other by time-reversal and are thus not split by an electrostatic perturbation, which is even under time reversal.

## 2.4 Spin-orbit interaction

In the first transition group elements the outermost 3d electrons are exposed to the surroundings, and therefore the interaction with the crystalline field is quite strong and in many cases stronger than the spin-orbit interaction. On the other hand, in the case of

TABLE 2.2  
 Notation and transformation properties  
 of atomic orbitals under crystalline fields  
 of different symmetries

Atomic Orbital	Octa- hedral $O_h$	Tetra- hedral $T_d$	Square planar $D_{4h}$	Low sym- metry $D_{2h}=D_{2xi}$
s	$a_{1g}$	$a_1$	$a_{1g}$	
$p_x$				
$p_y$	$t_{1u}$	$t_2$	$e_u$	
$p_z$			$a_{2u}$	
$d_{xy}$			$b_{2g}$	$B_1$
$d_{xz}$	$t_{2g}$		$e_g$	$B_2$
$d_{yz}$				$B_3$
$d_{z^2}$			$a_{1g}$	$A$
$d_{x^2-y^2}$	$e_g$	$e$	$b_{1g}$	

rare earth ions, the 4s electrons are shielded from the surroundings by  $5s^2 5p^6$  electrons and therefore are less affected by the crystal field. In this case spin-orbit interaction is stronger than crystalline field interaction. Therefore there are two interactions which vie with each other, one the spin-orbit coupling and the other the interaction of crystalline field with the orbital motion. The spatial degeneracy is partly lifted when the latter interaction is stronger than the former. In the iron group of transition elements this is of the order of  $20,000 \text{ cm}^{-1}$ . Depending upon its strength, the spin-orbit coupling causes a little of the orbital magnetic moment to be admixed with the spin so that the behaviour in a magnetic field is modified.

## 2.5 Spin-Hamiltonian

The magnetic properties of an ionic complex in a crystal field are intimately connected with the energy levels of the ion. For complexes of the first transition group the magnitude of the potential  $V$  provided by the ligands<sup>2</sup> is such as to make

$$\lambda(r) \underline{l} \cdot \underline{s} < V < e^2/r_{ij}$$

The potential  $V$  provided by the ligands can be expressed as<sup>2</sup>

$$V = V(R) + V_o$$

where  $V_R$  spans the  $a_{1g}$  representation in the group  $O_h$ .

$V_0$  expanded in Cartesian coordinates is

$$x^4 + y^4 + z^4 - \frac{3}{5} r^4$$

The results of electron paramagnetic resonance experiments are interpreted on the basis of a model of several magnetic complexes related to each other through a specific point group symmetry elements of the local sublattice. To study the problem one has to consider the dominant terms in the Hamiltonian. In the order of decreasing magnitude these are given in Table 2.3 for the salts containing iron group elements as impurities.<sup>1-5</sup>

Levels more than  $10^3 \text{ cm}^{-1}$  above the ground level can be neglected at room temperatures as they are insufficiently populated to give an absorption spectrum. Thus we are left with the lowest group of levels of the free-ion Hamiltonian which is characterised by orbital and spin angular quantum numbers  $L$  and  $S$  and is described by Russell-Saunders's coupling.

The 3d-ion configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^n$  where  $n$  varies from 1 to 9 is taken for granted to classify  $\mathcal{H}_0$  energy level (Table 2.3). To explain certain features such as hyperfine structure, configurational mixing is taken into consideration. This enables one to treat  $1s^2 2s^2 2p^6 3s^2 3p^6$  closed shell with  $L=S=0$  as diamagnetic. For paramagnetic ions of iron group  $n$  is non-zero. For  $\text{Mn}^{2+}$   $n=5$ ,  $L=0, S=5/2$  while for  $\text{V}^{4+}$   $n=1$ ,  $L=2, S=1/2$  and we have

TABLE 2.3

Dominant Terms in the Hamiltonian  
for salts of Iron Group Transition Metals

Sub-Hamiltonian $H_{\text{sub}}$	Magnitude of the Energy ( $\text{cm}^{-1}$ )	Symbol
Free Ion Energy (spin-independent)	$10^5$	$(\mathcal{H}_1) W_F = \sum_k \left( \frac{p_k^2}{2m} - \frac{ze^2}{r_k} \right) + \sum_{j < k} e^2 / r_{jk}$
Crystal Field	$10^4$	$(\mathcal{H}_2) V$
Spin-orbit Interaction	$10^2$	$(\mathcal{H}_3) W_{LS}$
Zeeman Term	1	$(\mathcal{H}_4) \beta \underline{H} \cdot (\underline{L} + 2\underline{S})$
Spin-spin Interaction	1	$(\mathcal{H}_5) W_{SS}$
Interaction with the nuclear field	$10^{-2}$	$(\mathcal{H}_6) W_{NN}$
Interaction with the external field	$10^{-3}$	$(\mathcal{H}_7) \chi \beta_N \cdot \underline{H} \cdot \underline{I}$

$(2L+1).(2S+1)$  energy levels which are degenerate. This degeneracy is partly lifted by a crystalline potential described already.

One interesting fact about the magnetic properties of the iron-group transition elements is that the leading contribution to the magnetic moment arises from the spin magnetic moment only. This allows us to introduce a fictitious spin  $S'$ , whose components are

$$S'_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$S'_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$S'_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

and the concept of spin Hamiltonian

$$\mathcal{H} = g\beta \underline{H} \cdot \underline{S} \quad \dots \quad (2.3)$$

To determine the energy perturbation in a magnetic field the eigen values of the spin Hamiltonian equation 2.3 are to be found. This concept of the spin Hamiltonian is due to Abragam and Pryce<sup>2</sup>. The lowest orbital  $|0\rangle$  contains a single electron in the ground state of the complex. Neglecting the spin-orbit coupling this may be represented by  $|0, \frac{1}{2}\rangle, |0, -\frac{1}{2}\rangle$ . The perturbation  $\lambda \hat{L} \cdot \hat{S}$  changes these states. The perturbed forms are:



$$|0, \frac{1}{2}\rangle + c |1, -\frac{1}{2}\rangle = | " \frac{1}{2} " \rangle$$

$$|0, -\frac{1}{2}\rangle + c |-1, \frac{1}{2}\rangle = | " -\frac{1}{2} " \rangle$$

In the absence of a magnetic field these two states are degenerate and form a Kramers' doublet. Application of a magnetic field  $H_z$  in the direction of z-axis produces a perturbation  $\beta H_z (\hat{L}_z + 2\hat{S}_z)$ . The matrix elements of this perturbation and the states  $| " \pm \frac{1}{2} " \rangle$  determine the energy separation between the resulting pair of levels. The result is that the observable splitting is just what one would expect if we can completely ignore the orbital angular momentum and replace its effect by an anisotropic coupling between the electron spin and the magnetic field. As the g-tensor is derived by constructing the matrix of  $(\underline{L} + g_e \underline{S})$  for the states  $|+\rangle$  and  $|-\rangle$ , the spin-Hamiltonian is

$$\begin{aligned} \mathcal{H} &= \beta \underline{H} \cdot \underline{g} \cdot \underline{S} \\ &= \beta \{ g_{\parallel} H_z \hat{S}_z + g_{\perp} (H_x \hat{S}_x + H_y \hat{S}_y) \} \quad \dots \quad (2.4) \end{aligned}$$

where  $\hat{S}_x$ ,  $\hat{S}_y$  and  $\hat{S}_z$  are components of the fictitious spin  $\underline{S}$ . The states  $|+\rangle$  and  $|-\rangle$  are the eigenfunctions of  $\hat{S}_z$  with eigen values  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , respectively. The z-axis of the g-tensor coincides with the symmetry axis of the system. It follows that the spin-Hamiltonian is so-called since it operates on wave functions expressed in terms of spin variables only.

## 2.6 Applications of Spin Hamiltonian

The above considerations will now be applied to the specific case of an ion with a single 3d electron. The ground state of such an ion, (eg.  $\text{Ti}^{3+}$ ,  $\text{V}^{4+}$ ), is a D state. By spin-orbit coupling this splits into  ${}^2D_{3/2}$  and  ${}^2D_{5/2}$ , the former being lower. This is a valid classification in the crystalline complex as  $\mathcal{H}_2$  (=V) is stronger than  $\mathcal{H}_3$  (spin-orbit) and the free-ion spin-orbit coupling is completely broken. The spin-orbit interaction is represented by

$$\mathcal{H}_3 = \lambda \hat{\underline{L}} \cdot \hat{\underline{S}}$$

For a  $d^1$  system the shell is less than half-filled and, therefore,  $\lambda$  is positive. In the absence of an applied magnetic field, the lower  $t$  level of a  $d^1$  system is split into three Kramers' doublets because of either a crystalline field or spin-orbit coupling or both. Application of magnetic field at this stage amounts to introducing a perturbation  $\mathcal{H}_4$ :

$$\mathcal{H}_4 = \underline{H} \cdot (\hat{\underline{L}} + 2\hat{\underline{S}})$$

This interaction which is linear in magnetic field lifts the Kramers' degeneracy completely. In a paramagnetic resonance experiment only the lowest doublet is effective at the magnetic fields available in the laboratory and one absorption line results. This situation is shown in Fig. 2.4 for a crystalline field of rhombic

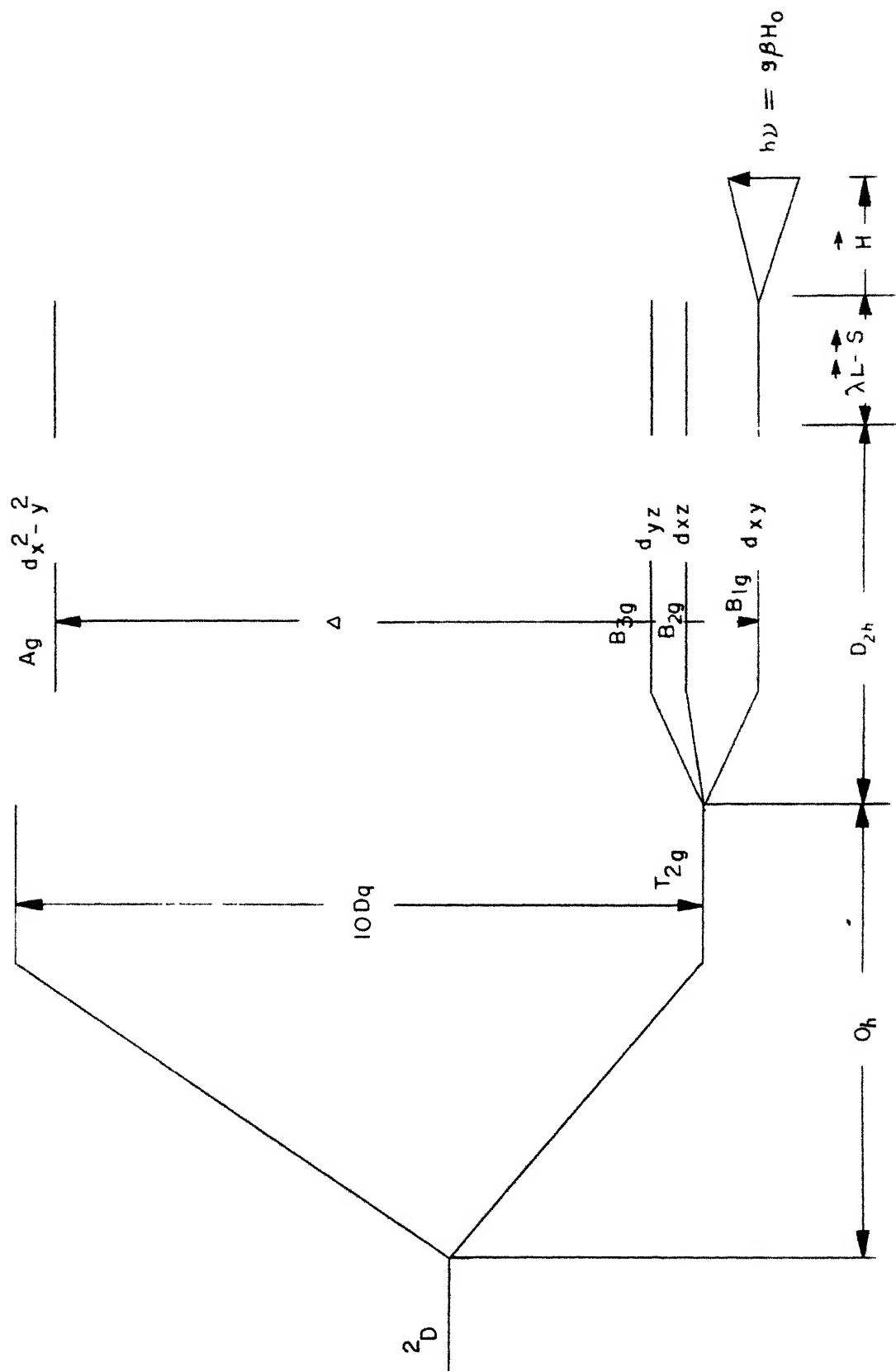


FIG. 2.4 REMOVAL OF DEGENERACY IN THE  $2D$  STATE ( $3d^1$  CONFIGURATION) OF  $VO^{++}$  ION BY VARIOUS PERTURBATIONS (HYPERFINE COUPLING  $\vec{I} \cdot \vec{S}$  OF THE ELECTRON AND  $V^{51}$  NUCLEAR SPINS IS NOT SHOWN)

symmetry. However, due to the hyperfine interaction with the nucleus each of the two levels is further split into  $(2I+1)$  levels where  $I$  is the spin of metal ion nucleus. For example in the case of  $V^{4+}$ ,  $I=7/2$  and this results in an eight line hyperfine spectrum, (Fig.6.1).

## 2.7 S-State Ions

The paramagnetic spectrum of divalent manganese ion in crystalline media is more complicated and theoretically more interesting. The ground state of the free ion  $Mn^{2+}$  is six-fold degenerate, the spectroscopic classification being  $(d^5)^6S_{5/2}$ . It is important to note that a pure  $^6S_{5/2}$  manifold is not split by the perturbation  $\mathcal{H}_2$  since an electric field is spin-independent and  $^6S_{5/2}$  is an orbital singlet. However, if a divalent manganese ion is placed in a crystal environment of cubic symmetry, the electron paramagnetic resonance spectrum shows<sup>3</sup> that the octohedral cubic field splits the free-ion ground-state manifold into two levels: the upper four-fold degenerate state  $\Gamma_8$ , the lower two-fold degenerate state  $\Gamma_7$ . This ground state splitting  $(\Gamma_8 - \Gamma_7)$  can be accounted for qualitatively by observing that because of the presence of spin-orbit interaction the ground state is not a pure  $^6S_{5/2}$ . If the cubic field environment is regarded as equivalent to an electric field with cubic symmetry, it follows from symmetry arguments<sup>4</sup> that such a manifold

is split by a cubic perturbation into sub-manifolds of 2 and 4. Thus the splitting in  $\text{Mn}^{2+}(^6\text{S}_{5/2})$  arises as the free ion spin-orbit coupling mixes together states with the same J-value. For instance,  $^6\text{S}_{5/2}$  can mix with  $^4\text{P}_{5/2}$  and  $^4\text{P}_{5/2}$  with  $^2\text{D}_{5/2}$ . If the crystalline field has a symmetry lower than the cubic, further distortions split the quartet into two more doublets and in all one has three doublets with Kramers' degeneracy. An external magnetic field removes this degeneracy and six levels result. Magnetic dipole transitions among these six levels give rise to five absorption lines, which is the so-called fine structure of EPR spectrum, (Fig. 2.5). The nucleus of  $\text{Mn}^{55}$  has a spin of 5/2 and the hyperfine interaction causes each of the six fine structure levels split into six levels giving rise to a total of 36 levels. This results, using the selection rules  $\Delta M_S = \pm 1$  and  $\Delta m_I = 0$ , in a 5x6 (=30) lines in the EPR spectrum of  $\text{Mn}^{2+}$  placed in a crystal field of symmetry lower than cubic.

## 2.8 Hyperfine Structure

Hyperfine interactions are mainly magnetic dipole interactions between the electronic magnetic moment and the nuclear magnetic moment of the paramagnetic ion, neglecting the nuclear moments of neighbouring ions. In the case of s-electrons it is the Fermi contact interaction which is important. The octet in

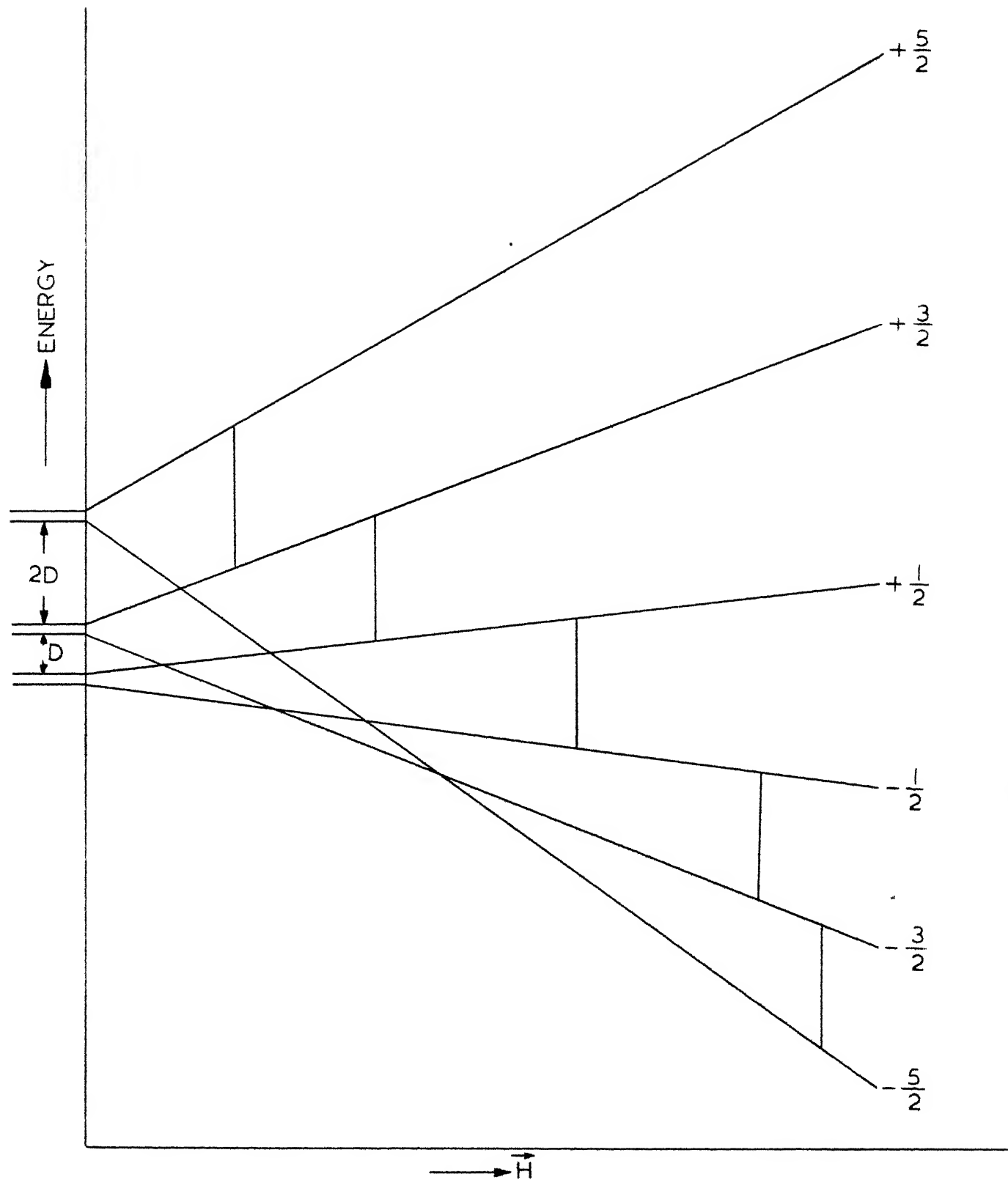


FIG.2.5 ZERO-FIELD SPLITTING BETWEEN THE THREE KRAMERS' DOUBLETS OF A SEXTET STATE IN THE  $Mn^{2+}$  ION LEADING TO FINE STRUCTURE IN EPR SPECTRUM. (HYPERFINE INTERACTION DUE TO  $Mn^{55}$  NUCLEUS NOT SHOWN)

the EPR of vanadyl ion and the sextets in the EPR of divalent manganese are the result of hyperfine interactions. The classical expression for the potential energy  $V_{ij}$  of magnetic interaction between two magnetic dipoles of moments  $\vec{\mu}_i$  and  $\vec{\mu}_j$  a distance  $\vec{r}_{ij}$  apart, is:

$$V_{ij} = \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3} - \frac{3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \quad \dots (2.5)$$

Expression (2.5), treated as an operator, and summed over all neighbours, is the dipole-dipole interaction term in the Hamiltonian. In our effective spin-Hamiltonian we attempt to relate the electronic moment to the spin vector  $\underline{S}$ . Abragam et al<sup>2</sup> described the nuclear hyperfine structure by the following Hamiltonian:

$$\mathcal{H} = \gamma_e \gamma_n \left[ \frac{3(\underline{I} \cdot \underline{r})(\underline{r} \cdot \underline{S})}{r^5} - \frac{\underline{S} \cdot \underline{I}}{r^3} + \frac{\underline{L} \cdot \underline{I}}{r^3} + \frac{8\pi}{3} \delta(\underline{r}) \cdot (\underline{S} \cdot \underline{I}) \right] \quad \dots (2.6)$$

The first two terms in this expression correspond to the dipolar interaction between the electronic and nuclear magnetic moments. The third term gives the contribution resulting from the orbital motion of the electron while the last term describes the Fermi contact interaction<sup>5</sup>. Interactions in Equation (2.6) depend mainly on that part of the wave function which is near to the nucleus.

Introducing a tensor operator  $\hat{\underline{A}}$  analogous to  $\hat{\underline{g}}$  tensor, (2.6) can also be written as

$$\mathcal{H}_{\text{hyperfine}} = A_x \hat{I}_x \hat{S}_x + A_y \hat{I}_y \hat{S}_y + A_z \hat{I}_z \hat{S}_z$$

in a principal axis system. In general, the electron-nucleus hyperfine interaction is represented by  $\hat{\underline{S}} \cdot \hat{\underline{T}} \cdot \hat{\underline{I}}$  where  $\underline{T}$  is the hyperfine tensor. This can be written as the sum

$$a \hat{\underline{S}} \cdot \hat{\underline{I}} + \hat{\underline{S}} \cdot \hat{\underline{T}}' \cdot \hat{\underline{I}} \quad \dots (2.7)$$

where  $a$  is the isotropic part and  $\underline{T}'$  is the magnetic dipolar tensor. In the system  $\text{VO}^{2+}:\text{Cs}_2\text{SO}_4$  described in chapter 4 of this thesis the anisotropic splittings which are due to  $\underline{T}'$  are investigated in some detail.

## 2.9 Ligand Hyperfine Structure:

The spectrum of  $\text{Mn}^{2+}$  in the substitutional sites in NaF single crystal which has been studied in detail in this thesis in chapter 5 provides an extensive super-hyperfine structure (SHFS) in addition to the usually observed fine and hyperfine structure. This additional structure has been ascribed to the interaction of  $\text{F}^{19}$  nuclei with the localised spin magnetization of the  $\text{Mn}^{2+}$  ion and is described by the addition of the following sub-Hamiltonian:



$$\mathcal{H}^{19} = \sum_i \underline{S} \cdot \underline{A}^i \cdot \underline{I}_i \quad \dots (2.8)$$

where the summation is to be taken over the six neighbouring  $F^{19}$  nuclei each of spin  $\frac{1}{2}$ . This interaction splits each level into a number of sublevels to provide as many as fifteen new lines for each hyperfine line. Tinkham<sup>6</sup> ascribed this effect to covalent bonding between the metal ions and the fluorine ions. Stevens<sup>7</sup> and Griffiths and Owen<sup>8</sup> adopted this covalent bond theory while discussing the SHFS of  $Ir^{4+}$  ion in chloroplatinates. For octohedral complexes of  $MX_6$  type Owen suggested that the unpaired electrons responsible for the paramagnetism might be partially transferred from M to  $X_6$  in molecular orbitals which are usually of anti-bonding type. Shulman and Jaccarino<sup>10</sup> favoured the superexchange mechanisms discussed by Anderson<sup>11</sup>. Clogston et al<sup>12</sup> adopted the covalent bonding theory in their phenomenological description of the fluorine hyperfine interaction where the entire burden of the interaction rests upon the augmented d-wave functions. Fig. 2.6 shows schematic representation of bonding orbitals in an octohedral complex as described by Hall et al<sup>13</sup>.

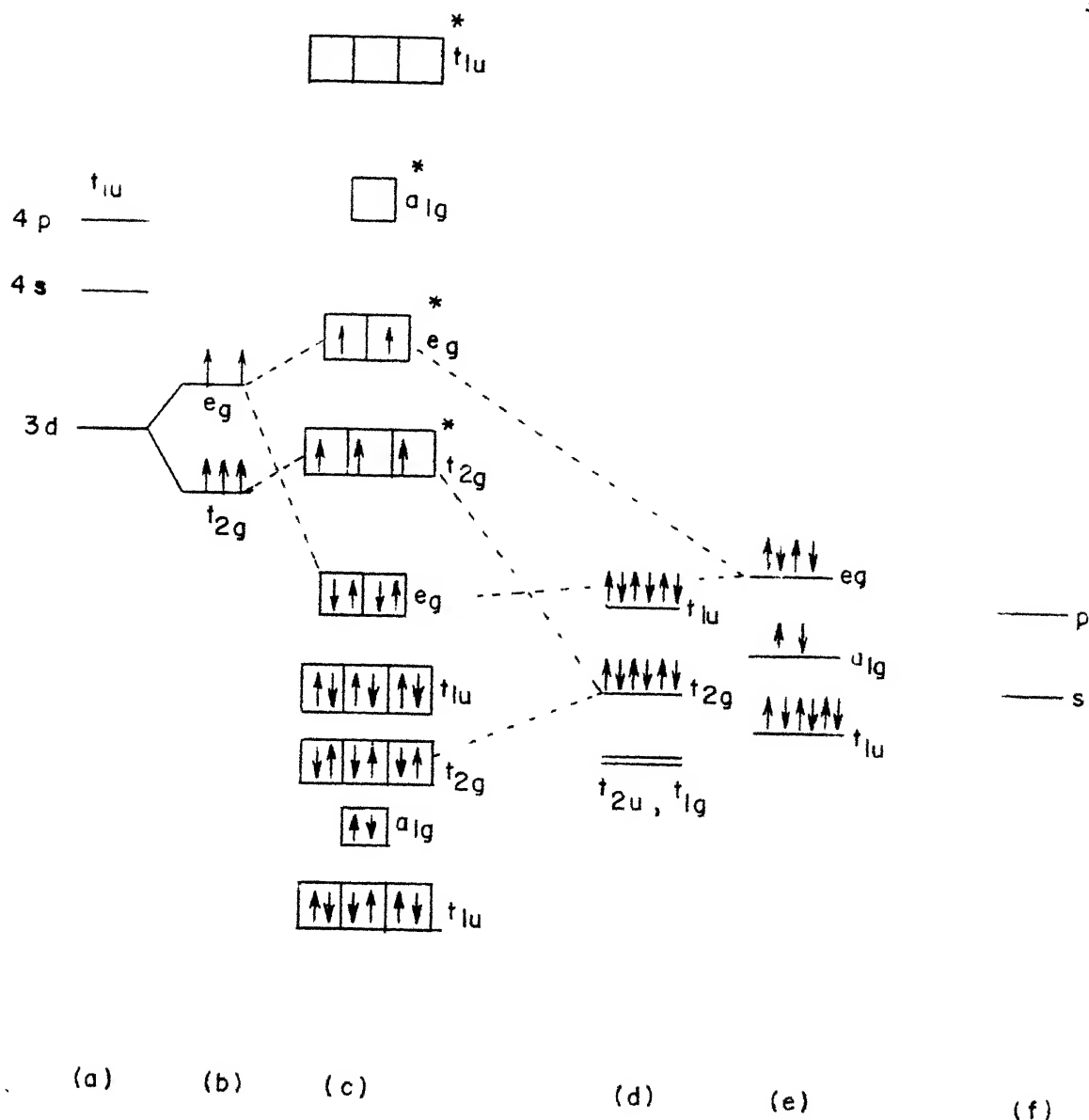


FIG. 2.6 BONDING ORBITALS IN AN OCTAHEDRAL COMPLEX. ARROWS INDICATE OCCUPATION OF THE LEVELS BY d-ELECTRON. ASTERISKS INDICATE ANTIBONDING ORBITALS.

- (a) ENERGY LEVELS OF FREE METALS ION
- (b) SPLITTING BY AN ELECTRIC FIELD OF  $O_h$  SYMMETRY
- (c) BONDING CENTRAL ION AND THE P-ORBITALS OF THE SURROUNDING LIGANDS
- (d)  $\pi$ -BONDING ORBITALS
- (e)  $\sigma$ -BONDING ORBITALS
- (f) ENERGY LEVELS OF FREE LIGAND IONS

## 2.10 Spin Hamiltonian Parameters

For a crystal with an ion embedded in it, in the absence of a theory to calculate parameters from first principles, paramagnetic resonance fields can be made to fit the spin Hamiltonian. Omitting nuclear terms which do not involve electron operators, the Zeeman interaction is taken into account by

$$\beta (g_x S_x H_x + g_y S_y H_y + g_z S_z H_z);$$

the fine structure is taken care of by the parameters  $D$  and  $E$  in

$$D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] + E (S_x^2 - S_y^2);$$

the hyperfine structure is accounted for by

$$A_z I_z S_z + A_x I_x S_x + A_y I_y S_y ;$$

and the ligand hyperfine structure, if present, is taken care of by equation (2.8).

## 2.11 EPR of Liquids

In the present study, the EPR spectra of  $VO^{2+}$  in alkali chlorides show certain features characteristic of liquids rather than solids. So it is felt necessary to briefly outline the theory of EPR spectra of liquids<sup>14</sup>.

The paramagnetic complexes in liquid solutions can be considered as microcrystals tumbling in a random way as they are jostled by the molecular motions of the solvent liquid. The immediate environment of the paramagnetic ion in these microcrystals can be as high as cubic with strong possibility of an axial component. In a coordinate system (p,q,r) fixed in the molecule the axial spin Hamiltonian can be written as <sup>14,15</sup>

$$\begin{aligned} \mathcal{H} = & \beta \left[ g_{\parallel} H_r S_r + g_{\perp} (H_p S_p + H_q S_q) \right] + D S_r^2 \\ & + A_{\parallel} I_r S_r + A_{\perp} (I_p S_p + I_q S_q) \end{aligned}$$

This can be transformed into laboratory coordinate system by using the following transformation equations:

$$\begin{aligned} H_r &= H_0 \cos \theta \\ S_r &= S_z \cos \theta + S_x \sin \theta \cos \phi \\ &\quad + S_y \sin \theta \sin \phi \\ &= S_z \cos \theta + \frac{1}{2}(S_+ e^{-i\phi} + S_- e^{+i\phi}) \sin \theta \end{aligned}$$

After transforming into the laboratory coordinate system x,y,z the Hamiltonian takes the form<sup>14,15</sup>

$$\begin{aligned}
\mathcal{H} = & g\beta H_0 S_z + a\mathbf{I}\cdot\mathbf{S} + (D/2).(3\cos^2\theta-1)S_z^2 \\
& + (D/2)\sin\theta\cos\theta \left[ (S_z S_+ + S_+ S_z)e^{-i\phi} \right. \\
& \left. + (S_z S_- + S_- S_z)e^{i\phi} \right] + (1/3).(\Delta g\beta H_0 + bI_z). \\
& (3\cos^2\theta-1)S_z \\
& + (b/2)\sin\theta\cos\theta(I_+e^{-i\phi} + I_-e^{i\phi})S_z \\
& + \frac{1}{2}(\Delta g\beta H_0 + bI_z)\sin\theta\cos\theta(S_+e^{-i\phi} + S_-e^{i\phi}) \\
& + (b/4)\sin^2\theta(I_+S_+e^{-2i\phi} + I_-S_-e^{2i\phi}) \\
& - (b/12).(3\cos^2\theta-1).(I_+S_- + I_-S_+) \quad \dots \quad (2.9)
\end{aligned}$$

where  $g = (1/3)(g_{\parallel} + 2g_{\perp})$ ,  $\Delta g = g_{\parallel} - g_{\perp}$

$$a = (1/3)(A + 2B), \quad b = A - B$$

with  $A = A_{\parallel}$  and  $B = A_{\perp}$  while  $I_{\pm}$  and  $S_{\pm}$  are the usual raising and lowering operators, operating on nuclear and electronic spin states respectively. As the molecule tumbles,  $\theta$  becomes time dependent, and the above

Hamiltonian (2.9) can be written as  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}(t)$ ,

where  $\mathcal{H}_0$  is time independent and isotropic and is given by the first two terms in the above Hamiltonian (2.9), viz.,  $g\beta H_0 S_z + a\mathbf{I}\cdot\mathbf{S}$ .  $\mathcal{H}(t)$  contains rest of the terms and is time dependent due to random time dependence of  $\theta$ . If the random motions are extremely rapid, which means, if the motional frequency times  $\hbar$  exceeds the interaction energy in question, the time dependent terms

average out to zero and have little effect. This is the limiting case of situation which can be seen in the experiment. In general, however, the time dependent terms lead to important effects. McConnell<sup>14</sup> has shown that the anisotropies in g and A terms, which are averaged out to zero due to rapid tumbling of the molecule,  $\langle \overline{g(t)} \rangle = 0$ , contribute to the line widths of the isotropic spectrum given by the Hamiltonian  $\mathcal{H}_0$ ; and the line widths are predicted to obey a formula of the type

$$\Delta\nu \sim 1/T_2 \simeq \tau_c (\Delta g \beta H_0 + b m_I)^2 / \hbar^2$$

where  $\tau_c$  is the correlation time, describing the random motion of the molecule. Rogers and Pake<sup>16</sup> first observed these line width effects in their study of EPR of  $VO^{2+}$  complexes in solutions. Similar effects are observed in the present study and are discussed in chapter 6 of this thesis.

## 2.12

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## CHAPTER III

ELECTRON PARAMAGNETIC RESONANCE OF  $Mn^{2+}$   
IN SINGLE CRYSTALS OF CAESIUM SULPHATE,  $Cs_2SO_4$

# ABSTRACT

The electron paramagnetic resonance (EPR) spectrum of divalent manganese ion has been studied at 9.5 Gc/sec. These studies reveal that  $\text{Mn}^{2+}$  substitutes  $\text{Cs}^+$  ion and the charge compensation is restored by formation of cation vacancies—the  $\text{Mn}^{2+}$  ion substitutes at a  $\beta\text{-Cs}^+$  site and gets associated itself with a vacancy at a nearest neighbour  $\beta\text{-Cs}^+$  site. This gives rise to a complex in the ab-crystallographic plane. All the spectra observed in the temperature range from room temperature (300 °K) to liquid nitrogen temperature (77 °K) have been described by the spin-Hamiltonian for  $\text{Mn}^{2+}$  in rhombic crystalline field. The temperature variation of the parameters D and E has been studied in the above temperature range. The spectra for the observed complex along its three principal axes have been analysed using second order perturbation equations. The relevant energy matrix is diagonalised to determine the influence of the off-diagonal elements which may be significant in the present case. The parameters which satisfy a least-square fit are:

$$g_z = 1.999(5), g_x = 2.014(9), g_y = 2.008(9);$$

$$A_z = -93 \text{ Oe}, A_x = -91 \text{ Oe}, A_y = -92 \text{ Oe};$$

$$D = -941 \text{ Oe}, E = -14 \text{ Oe};$$

$$b_4^0 = 0.0 \text{ Oe}, b_4^2 = 13 \text{ Oe}, b_4^4 = -77 \text{ Oe};$$

$$\phi = 25^\circ; \text{ where } \phi \text{ is the angle the direction of the complex making with the longest crystallographic axis } b \text{ in the ab-plane.}$$

### 3.1 INTRODUCTION

During the past few years the technique of electron paramagnetic resonance (EPR) has been used for studying impurity ions in alkali sulphates<sup>1-4</sup>. The value of EPR methods to study the phase transition<sup>3-7</sup> is well-known. Moreover, EPR has been an important structural tool in perovskites, spinels and garnets<sup>8</sup>. Chowdari and Venkateswarlu<sup>3</sup> found indications of a probable phase transition around -130 °C in Mn<sup>2+</sup> doped K<sub>2</sub>SO<sub>4</sub> single crystal. It was felt that it would be interesting to see whether such a transition occurs in the case of the isomorphous sulphates<sup>†</sup> which are not ferro-electric. Information about the lattice defects such as positive ion vacancies is valuable for the solid state studies in general. In the present studies Mn<sup>2+</sup> which is an S-state ion belonging to the iron group transition elements is doped in single crystals of caesium sulphate which is not ferroelectric. Exhaustive analysis of the observed paramagnetic resonance spectra is made in the temperature range of 77 °K to 300 °K and the spin-Hamiltonian parameters of the system Mn<sup>2+</sup>:Cs<sub>2</sub>SO<sub>4</sub> for the observed complex in the ab-crystallographic plane have been obtained. To our knowledge such studies have not been reported in the literature.

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<sup>†</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is known to become ferroelectric<sup>4</sup> below -50 °C.

## 3.2

## CRYSTAL STRUCTURE

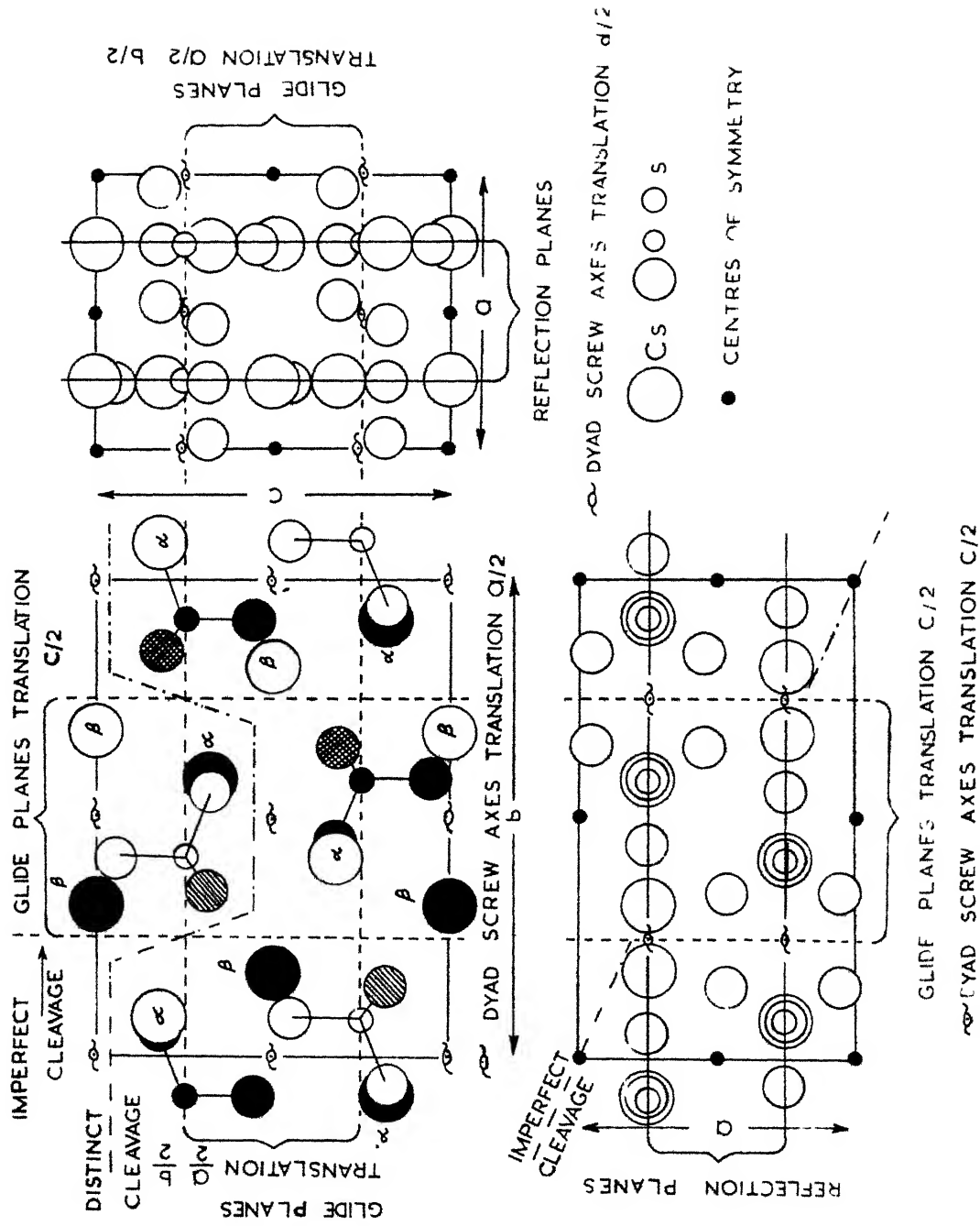
The crystal structures of isomorphous sulphates of potassium, ammonium, rubidium and caesium have been determined by Ogg<sup>9</sup>. They belong to the symmetry group  $V_h^{16}$  and contain two reflection planes, four glide planes, twelve dyad screw axes, and sets of four centres of symmetry. The orthorhombic unit cell dimensions are

$$a = 6.218 \overset{\circ}{\text{\AA}}$$

$$b = 10.884 \overset{\circ}{\text{\AA}}$$

$$c = 8.198 \overset{\circ}{\text{\AA}}$$

The structure of  $\text{Cs}_2\text{SO}_4$  consists of layers of atoms parallel to (100) planes the spacing between which is  $a/2$ . The reflection planes are  $(100)_{1/4}$  and  $(100)_{-1/4}$  if we assume the origin of coordinates is at the centre of the unit cell. The unit cell contains four formula weights. Depending on the oxygen environment the caesium atoms are classified as  $\alpha$ - or  $\beta$ -type<sup>9</sup>. As a result there are four caesium ions of  $\alpha$ -type and four caesium ions of  $\beta$ -type in the unit cell (Fig. 3.1). A knowledge of the positions of caesium atoms is necessary to interpret the various paramagnetic resonance spectra described in this work.



G.3.1. APPROXIMATE POSITIONS OF ATOMS AND SYMMETRIES OF  $Cs_2SO_4$  IN THE THREE PRINCIPAL PLACES (AFTER A OGG<sup>10</sup>)

## 3.3

## EXPERIMENTAL

Caesium sulphate supplied by E. Merck and of analytical grade has been used. 0.3 mole percent of  $\text{MnSO}_4$  has been added to a saturated aqueous solution of  $\text{Cs}_2\text{SO}_4$ . Slow evaporation yielded thin plates of transparent crystals, 1cm x 1cm x 0.2cm size, with well-developed  $\{001\}$  faces. Spectrophotometric analysis of the experimental crystal showed that the manganese content is less than 1250 parts per million. The crystal has no detectable traces of water either to give infra-red absorption bands on Cary-14 spectrophotometer or proton resonance signal on wide line NMR. Desired orientation of the experimental crystal with respect to the magnetic field has been easy because of the known axes  $\langle 001 \rangle$  and  $\langle 100 \rangle$  the former being perpendicular to the well-developed face of the crystal while the latter being the needle axis. X-ray rotation photographs taken along these directions confirmed the assignment of the axes. Measurements have been made at x-band with a Varian V-4502 EPR spectrometer having a 9-inch rotating magnet and 100 kc/sec field modulation. A Varian rotating cavity V-4533 has been used to determine the angular variation and the direction of the principal axes of the g-tensor. A speck of polycrystalline diphenylpicrylhydrazyl (DPPH) whose g-value is taken as  $2.0036^{10}$  placed alongside the crystal has been used as a field marker. The

magnetic field has been standardised using proton resonance in conjunction with a nuclear flux meter F-9 and Beckman 10-110 Mc convertor 7571. Temperature variation experiments have been done using a Varian V-4530 temperature controller. The spectrometer has been operated at low power the microwave power being one milliwatt.

### 3.4 THEORY

The ground state of  $\text{Mn}^{2+}$  with its  $3d^5$  configuration is  ${}^6S_{5/2}$ . In a crystal field of low symmetry such as  $\text{Cs}_2\text{SO}_4$  excited quartet levels get admixed into the ground state<sup>11</sup> and the ground state is split into three Kramers' doublets. In a magnetic field the degeneracy is completely removed and five fine structure transitions are possible. Due to the interaction with the nucleus of spin 5/2 each electronic transition gives rise to six hyperfine transitions. Thus the electron paramagnetic resonance absorption of  $\text{Mn}^{2+}$  in caesium sulphate is expected to contain thirty lines. In general, the spectrum has more lines due to the presence of angular parts due to  $\text{Mn}^{2+}$  ions in equivalent positions or at different sites. Additional lines due to forbidden transitions are also possible.

The thirty line EPR spectra of  $\text{Mn}^{2+}$  obtained in the present case have been analysed using a more general spin-Hamiltonian appropriate to the low symmetry:

$$\begin{aligned}
\mathcal{H} = & g_z \beta H_z S_z + g_x \beta H_x S_x + g_y \beta H_y S_y + \frac{1}{3} b_2^0 0_2^0 + \frac{1}{3} b_2^2 0_2^2 \\
& + \frac{1}{60} b_4^0 0_4^0 + \frac{1}{60} b_4^2 0_4^2 + \frac{1}{60} b_4^4 0_4^4 \\
& + A S_z I_z + B S_x I_x + C S_y I_y \quad \dots \quad (3.1)
\end{aligned}$$

The operators  $O_n^m$  are given in an explicit form by Orbach<sup>12</sup> and  $g$ ,  $b_i^k$  are parameters to be fixed by experiment. The matrix of this spin-Hamiltonian (3.1)<sup>13</sup> in the manifold of  $S=5/2$  was diagonalised to a second order and the following expressions<sup>3,13</sup> have been used to calculate the fine structure positions at resonance when  $H \parallel z$ . The usual parameters  $D$ ,  $E$  and  $a$  replace the constants  $b_2^0$ ,  $\frac{1}{3}b_2^2$  and  $2b_4^0$  respectively.<sup>14</sup>

$$\begin{aligned}
H_1 (M=5/2 \leftrightarrow 3/2) &= H_0 - 4D + 9E^2/(H_1+D) - 5E^2/(H_1+3D) \\
&\quad - 2a - 3Eb_4^2/H_0 \\
H_2 (M=3/2 \leftrightarrow 1/2) &= H_0 - 2D - 9E^2/(H_2+D) + 9E^2/(H_2-D) \\
&\quad - 5E^2/(H_2+3D) + 5/2(a) - 1.5Eb_4^2/H_0 \\
&\quad - \frac{(b_4^4)^2}{20H_0}
\end{aligned}$$

$$\begin{aligned}
H_3 (M=1/2 \leftrightarrow -1/2) &= H_0 - 9E^2/(H_3-D) + 5E^2/(H_3+3D) \\
&\quad + 5E^2/(H_3-3D) - 9E^2/(H_3+D) \\
&\quad + 6Eb_4^2/H_0
\end{aligned}$$



$$\begin{aligned}
H_4(M = -1/2 \leftrightarrow -3/2) &= H_0 + 2D + 9E^2/(H_4 + D) - 9E^2/(H_4 - D) \\
&\quad - 5E^2/(H_4 - 3D) - 5/2(a) \\
&\quad - 1.5Eb_4^2/H_0 - \frac{(b_4^4)^2}{20H_0}
\end{aligned}$$

$$\begin{aligned}
H_5(M = -3/2 \leftrightarrow -5/2) &= H_0 + 4D + 9E^2/(H_5 - D) - 5E^2/(H_5 - 3D) \\
&\quad + 2a - 3Eb_4^2/H_0 \quad \dots \quad (3.2)
\end{aligned}$$

To take account of the hyperfine structure a term HFS has been added to each of the above equations (3.2):

$$\begin{aligned}
\text{HFS} &= -Am - \frac{B^2 + C^2}{4H_0} \{I(I+1) - m^2\} - \{(2M-1)m\}BC/H_0 \dots (3.2a) \\
&= H(m \leftrightarrow m)
\end{aligned}$$

The same expressions have been used cyclically when the static field  $H$  is parallel to  $x$  or  $y$ . The corresponding  $D^*, E^*, a^*, b_4^{2*}$  and  $b_4^{4*}$  are related by standard transformation relations listed in Table (3.1).  $A, B$  and  $C$  are hyperfine constants when  $H \parallel z$ ,  $H \parallel x$  and  $H \parallel y$  respectively.

To keep up the generality a term containing  $Q$  is usually added to the Hamiltonian (3.1) to take account of the quadrupole interaction. The contribution due to this to HFS in  $\theta = 90^\circ$  part of the spectrum is the addition of the extra term<sup>15</sup>

$$\frac{-Q^2 m.2 \{I(I+1)\} - 2m^2 - 1}{8BM(M-1)} \quad \dots \quad (3.2b)$$

TABLE 3.1

Relationship<sup>†</sup> among the constants of the spin-Hamiltonian for three mutually perpendicular orientations of the magnetic field H

Effective value of the constants	H    z	H    x	H    y
D* ( $b_2^{o*}$ )	D ( $\equiv b_2^o$ )	$\frac{1}{2}(-D+3E)$ ( $\equiv -\frac{1}{2}(b_2^o - b_2^2)$ )	$-\frac{1}{2}(D+3E)$ ( $\equiv -\frac{1}{2}(b_2^o + b_2^2)$ )
E* ( $\equiv b_2^{o*}$ )	E ( $\equiv b_2^2/3$ )	$-\frac{1}{2}(D+E)$ ( $\equiv -(3b_2^o + b_2^2)/6$ )	$\frac{1}{2}(D-E)$ ( $\equiv (3b_2^o - b_2^2)/6$ )
$b_4^{o*}$ ( $\equiv a^*/2$ )	$b_4^o$ ( $a/2$ )	$\frac{1}{6}(3b_4^o + b_4^2 + b_4^4)$	$\frac{1}{6}(3b_4^o - b_4^2 + b_4^4)$
$b_4^{2*}$	$b_4^2$	$-\frac{1}{2}(5b_4^o + b_4^2 - b_4^4)$	$-\frac{1}{2}(5b_4^o - b_4^2 - b_4^4)$
$b_4^{4*}$	$b_4^4$	$\frac{1}{6}(35b_4^o - 7b_4^2 + b_4^4)$	$\frac{1}{6}(35b_4^o + 7b_4^2 + b_4^4)$
A*	A	B	C
B*	B	C	A
C*	C	A	B
g*	$g_z$	$g_x$	$g_y$

<sup>†</sup> We are thankful to Dr. Daniel Schechter of Solid State Physics Laboratory, TRW Systems, for kindly sending a memo which discussed in detail the effects of interchanging site axes.

For manganese  $I=5/2$  so that  $m$  takes the values  $-5/2$  to  $+5/2$ . However, this term (3.2b) has been neglected in the present analysis as the quadrupole effects are found to be negligible.

The spin-Hamiltonian parameters obtained by using relations obtained with the help of second order perturbation theory are not necessarily correct as the validity of the use of the perturbation theory when the parameters form a sizable percentage of the fields at which resonance occurs is open to question. So they have been improved upon by diagonalising the relevant energy matrix for the case when  $E/D$  is a minimum. Taking the  $z$ -axis as the axis of quantisation one can see that the off-diagonal elements for  $H_x g_x S_x$  and  $H_y g_y S_y$  in equation (3.1) do not exist. The diagonal elements involve terms containing  $g_z H_z S_z, D, a$  and  $A_z$ . The off-diagonal elements due to  $E(S_x^2 - S_y^2)$  and  $A_x S_x I_x + A_y S_y I_y$  have been evaluated. To keep up the generality, the components  $A_x, A_y$  and  $A_z$  are all assumed to be different in this work. The off-diagonal elements in  $A_x$  and  $A_y$  have been obtained using the following relations:

$$\begin{aligned}
\langle M, m | A_x S_x I_x | N, n \rangle = A_x / 4 \{ & \delta_{M, N+1} \sqrt{S(S+1) - N(N+1)} + \\
& \delta_{M, N-1} \sqrt{S(S+1) - N(N-1)} \} \times \\
& \{ \delta_{m, n+1} \sqrt{I(I+1) - n(n+1)} + \\
& \delta_{m, n-1} \sqrt{I(I+1) - n(n-1)} \}
\end{aligned}$$

$$\begin{aligned}
\langle M, m | A_y S_y I_y | N, n \rangle = -A_y / 4 \{ & \delta_{M, N+1} \sqrt{S(S+1) - N(N+1)} - \\
& \delta_{M, N-1} \sqrt{S(S+1) - N(N-1)} \} \times \\
& \{ \delta_{m, n+1} \sqrt{I(I+1) - n(n+1)} - \\
& \delta_{m, n-1} \sqrt{I(I+1) - n(n-1)} \}
\end{aligned}$$

The elements of  $(2S+1).(2I+1)$  matrix with  $S=I=5/2$  are shown in Table (3.2).

M1		$+5/2$	$+3/2$	$+1/2$	$-1/2$	$-3/2$	$-5/2$
	$m$	$5/2, 3/2, 1/2, -1/2, -3/2, -5/2$	$3/2, 1/2, -1/2, -3/2, -5/2$	$1/2, -1/2, -3/2, -5/2$	$5/2, 3/2, 1/2, -1/2, -3/2, -5/2$	$3/2, 1/2, -1/2, -3/2, -5/2$	$1/2, -1/2, -3/2, -5/2$
$x(1, J)$	$5/2$	1					
$+5/2$	$3/2$	2					
	$1/2$	3					
	$-1/2$	4					
	$-3/2$	5					
	$-5/2$	6					
$+3/2$	$5/2$	37	7				
	$3/2$	62	38	8			
	$1/2$	63	39	9			
	$-1/2$	64	40	10			
	$-3/2$	65	41	11			
	$-5/2$	66	12				
$+1/2$	$5/2$	67	42	13			
	$3/2$	68	43	14			
	$1/2$	69	44	15			
	$-1/2$	70	45	16			
	$-3/2$	71	46	17			
	$-5/2$	72	47	18			
$-1/2$	$5/2$	93	48	19			
	$3/2$	94	49	20			
	$1/2$	95	50	21			
	$-1/2$	96	51	22			
	$-3/2$	97	52	23			
	$-5/2$	98	53	24			
$-3/2$	$5/2$	M	99	54	25		
	$3/2$	N	A	55	26		
	$1/2$	O	B	56	27		
	$-1/2$	P	C	57	28		
	$-3/2$	Q	D	58	29		
	$-5/2$		E	59	30		
$-5/2$	$5/2$		R	F	57	31	
	$3/2$		S	G	58	32	
	$1/2$		T	H	59	33	
	$-1/2$		U	I	60	34	
	$-3/2$		V	J	61	35	
	$-5/2$		W	K	62	36	

TABLE 3.2

MATRIX FOR EVALUATING THE ENERGY LEVELS IN THE EPR SPECTRUM OF  $Mn^{2+}$  in  $Ca_2SO_4$

TABLE 3.2

The 36x36 Matrix connected with  
the Energy Levels of EPR Spectrum

Numbered square	Matrix Element	Value
Diagonal elements 1-36		
1	x(1,1)	$2.5H_0 + 10/3.D + 6.25A + b_4^0$
2	x(2,2)	$2.5H_0 + 10/3.D + 3.75A + b_4^0$
3	x(3,3)	$2.5H_0 + 10/3.D + 1.25A + b_4^0$
4	x(4,4)	$2.5H_0 + 10/3.D - 1.25A + b_4^0$
5	x(5,5)	$2.5H_0 + 10/3.D - 3.75A + b_4^0$
6	x(6,6)	$2.5H_0 + 10/3.D - 6.25A + b_4^0$
7	x(7,7)	$1.5H_0 - 2/3.D + 3.75A - 3b_4^0$
8	x(8,8)	$1.5H_0 - 2/3.D + 2.25A - 3b_4^0$
9	x(9,9)	$1.5H_0 - 2/3.D + 0.75A - 3b_4^0$
10	x(10,10)	$1.5H_0 - 2/3.D - 0.75A - 3b_4^0$
11	x(11,11)	$1.5H_0 - 2/3.D - 2.25A - 3b_4^0$
12	x(12,12)	$1.5H_0 - 2/3.D - 3.75A - 3b_4^0$
13	x(13,13)	$0.5H_0 - 8/3.D + 1.25A + 2b_4^0$
14	x(14,14)	$0.5H_0 - 8/3.D + 0.75A + 2b_4^0$
15	x(15,15)	$0.5H_0 - 8/3.D + 0.25A + 2b_4^0$
16	x(16,16)	$0.5H_0 - 8/3.D - 0.25A + 2b_4^0$
17	x(17,17)	$0.5H_0 - 8/3.D - 0.75A + 2b_4^0$
18	x(18,18)	$0.5H_0 - 8/3.D - 1.25A + 2b_4^0$
19	x(19,19)	$-0.5H_0 - 8/3.D - 1.25A + 2b_4^0$
20	x(20,20)	$-0.5H_0 - 8/3.D - 0.75A + 2b_4^0$

TABLE 3.2 (CONTINUED)

Numbered square	Matrix Element	Value
21	$x(21,21)$	$-0.5H_0 - 8/3.D - 0.25A + 2b_4^0$
22	$x(22,22)$	$-0.5H_0 - 8/3.D + 0.25A + 2b_4^0$
23	$x(23,23)$	$-0.5H_0 - 8/3.D + 0.75A + 2b_4^0$
24	$x(24,24)$	$-0.5H_0 - 8/3.D + 1.25A + 2b_4^0$
25	$x(25,25)$	$-1.5H_0 - 2/3.D - 3.75A - 3b_4^0$
26	$x(26,26)$	$-1.5H_0 - 2/3.D - 2.25A - 3b_4^0$
27	$x(27,27)$	$-1.5H_0 - 2/3.D - 0.75A - 3b_4^0$
28	$x(28,28)$	$-1.5H_0 - 2/3.D + 0.75A - 3b_4^0$
29	$x(29,29)$	$-1.5H_0 - 2/3.D + 2.25A - 3b_4^0$
30	$x(30,30)$	$-1.5H_0 - 2/3.D + 3.75A - 3b_4^0$
31	$x(31,31)$	$-2.5H_0 + 10/3.D - 6.25A + b_4^0$
32	$x(32,32)$	$-2.5H_0 + 10/3.D - 3.75A + b_4^0$
33	$x(33,33)$	$-2.5H_0 + 10/3.D - 1.25A + b_4^0$
34	$x(34,34)$	$-2.5H_0 + 10/3.D + 1.25A + b_4^0$
35	$x(35,35)$	$-2.5H_0 + 10/3.D + 3.75A + b_4^0$
36	$x(36,36)$	$-2.5H_0 + 10/3.D + 6.25A + b_4^0$
Off-diagonal elements in (B + C) 37-61		
37	$x(7,2)$	$1.25(B + C)$
38	$x(8,3)$	$1.25(B + C)\sqrt{40}$
39	$x(9,4)$	$1.25(B + C)\sqrt{45}$
40	$x(10,5)$	$1.25(B + C)\sqrt{40}$
41	$x(11,6)$	$1.25(B + C)$
42	$x(13,8)$	$1.25(B + C)\sqrt{40}$
43	$x(14,9)$	$2(B + C)$

TABLE 3.2 (CONTINUED)

Numbered square	Matrix Element	Value
44	$x(15,10)$	$1.25(B + C)\sqrt{72}$
45	$x(16,11)$	$2(B + C)$
46	$x(17,12)$	$1.25(B + C)\sqrt{40}$
47	$x(19,14)$	$1.25(B + C)\sqrt{45}$
48	$x(20,15)$	$1.25(B + C)\sqrt{72}$
49	$x(21,16)$	$2.25(B + C)$
50	$x(22,17)$	$1.25(B + C)\sqrt{72}$
51	$x(23,18)$	$1.25(B + C)\sqrt{45}$
52	$x(25,20)$	$1.25(B + C)\sqrt{40}$
53	$x(26,21)$	$2(B + C)$
54	$x(27,22)$	$1.25(B + C)\sqrt{72}$
55	$x(28,23)$	$2(B + C)$
56	$x(29,24)$	$1.25(B + C)\sqrt{40}$
57	$x(31,26)$	$1.25(B + C)$
58	$x(32,27)$	$1.25(B + C)\sqrt{40}$
59	$x(33,28)$	$1.25(B + C)\sqrt{45}$
60	$x(34,29)$	$1.25(B + C)\sqrt{40}$
61	$x(35,30)$	$1.25(B + C)$
Off-diagonal elements in $(B - C)$ 62-86		
62	$x(8,1)$	$1.25(B - C)$
63	$x(9,2)$	$1.25(B - C)\sqrt{40}$
64	$x(10,3)$	$1.25(B - C)\sqrt{45}$
65	$x(11,4)$	$1.25(B - C)\sqrt{40}$
66	$x(12,5)$	$1.25(B - C)$
67	$x(14,7)$	$1.25(B - C)\sqrt{40}$
68	$x(15,8)$	$1.25(B - C)$
69	$x(16,9)$	$1.25(B - C)\sqrt{72}$
70	$x(17,10)$	$1.25(B - C)$
71	$x(18,11)$	$1.25(B - C)\sqrt{40}$



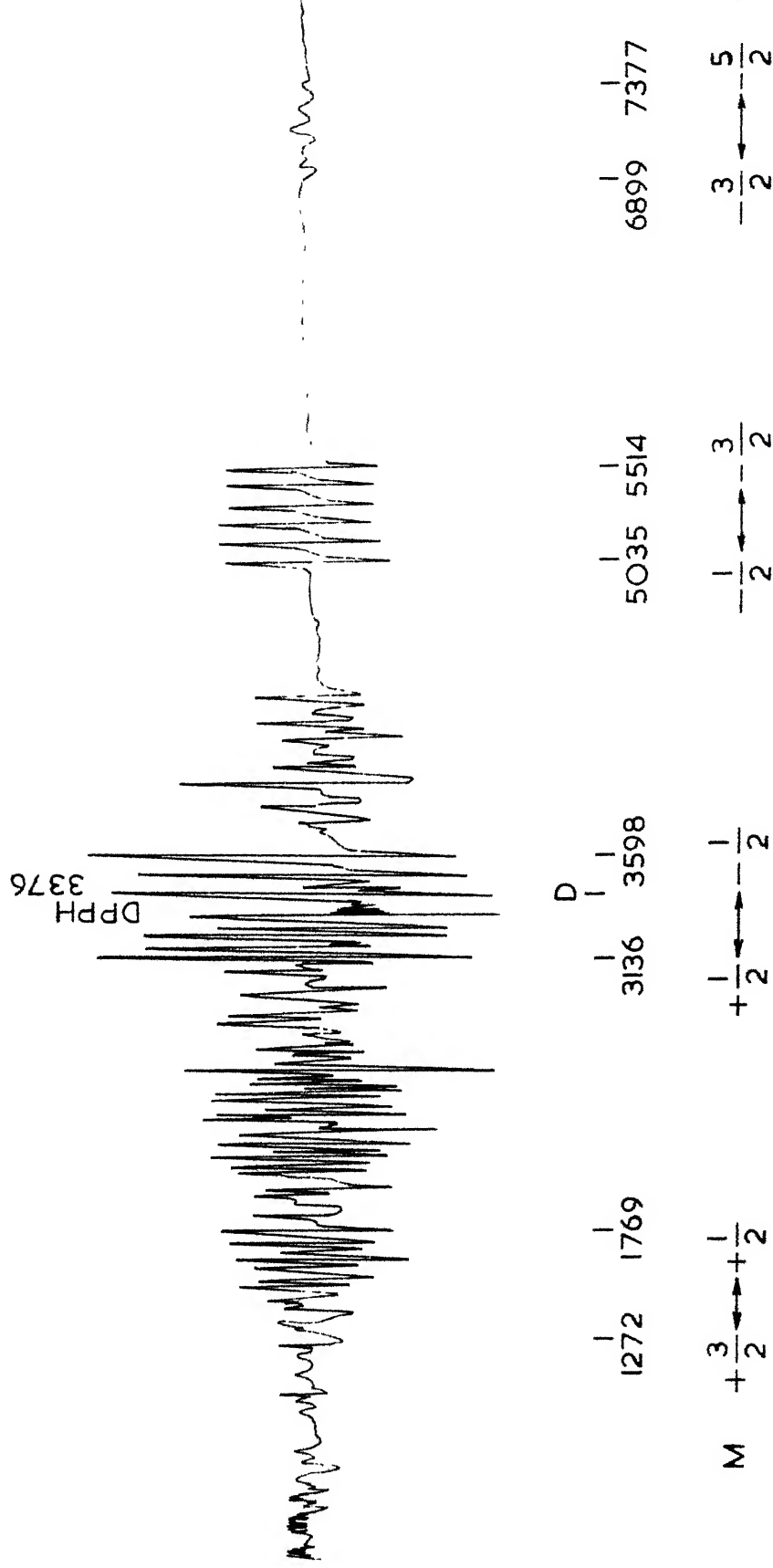


FIG.3-2 EPR SPECTRUM OF  $Mn^{2+}$  IN  $Cs_2SO_4$  SINGLE CRYSTAL AT ROOM TEMPERATURE ( $20^\circ C$ ). THE DIRECTION OF THE MAGNETIC FIELD IS MAKING  $25^\circ$  WITH THE  $b$  AXIS OF THE CRYSTAL IN  $ab$  PLANE  $H//$  TO  $z$  AXIS. DPPH IS THE FIELD MARKER. NUMBERS INDICATE FIELD VALUE IN OERSTED

TABLE 3.2 (CONTINUED)

Numbered Matrix Element square		Value
98	x(24,12)	$3\sqrt{2}E - \sqrt{2}/4 \cdot b_4^2$
99	x(25,13)	$3\sqrt{2}E - \sqrt{2}/4 \cdot b_4^2$
A	x(26,14)	$3\sqrt{2}E - \sqrt{2}/4 \cdot b_4^2$
B	x(27,15)	$3\sqrt{2}E - \sqrt{2}/4 \cdot b_4^2$
C	x(28,16)	$3\sqrt{2}E - \sqrt{2}/4 \cdot b_4^2$
D	x(29,17)	$3\sqrt{2}E - \sqrt{2}/4 \cdot b_4^2$
E	x(30,18)	$3\sqrt{2}E - \sqrt{2}/4 \cdot b_4^2$
F	x(31,19)	$\sqrt{10}E + \sqrt{10}/20 \cdot b_4^2$
G	x(32,20)	$\sqrt{10}E + \sqrt{10}/20 \cdot b_4^2$
H	x(33,21)	$\sqrt{10}E + \sqrt{10}/20 \cdot b_4^2$
I	x(34,22)	$\sqrt{10}E + \sqrt{10}/20 \cdot b_4^2$
J	x(35,23)	$\sqrt{10}E + \sqrt{10}/20 \cdot b_4^2$
K	x(36,24)	$\sqrt{10}E + \sqrt{10}/20 \cdot b_4^2$
Off-diagonal elements in $b_4^4$		
L	x(25,1)	$b_4^4/\sqrt{5}$
M	x(26,2)	"
N	x(27,3)	"
O	x(28,4)	"
P	x(29,5)	"
Q	x(30,6)	"
R	x(31,7)	"
S	x(32,8)	"
T	x(33,9)	"
U	x(34,10)	"
V	x(35,11)	"
W	x(36,12)	"

### 3.5 RESULTS AND DISCUSSION

Angular variation studies when the magnetic field is swept in the ab plane with the c-axis of the crystal as rotation axis indicate the existence of four distinct spectra over a  $180^\circ$ -scan. These spectra can be grouped into two categories:

(i) two identical spectra which have been obtained when the magnetic field is making an angle of  $25^\circ$  with the b axis of the crystal on either side of it. Each one of them has been identified as the z-axis of the complex;

(ii) two identical spectra which have been obtained when the magnetic field is making an angle of  $65^\circ$  with the b-axis of the crystal on either side of it, each one of them having been identified as the y-axis of the complex.

Angular variation studies by rotating the magnetic field in the bc plane with the shortest axis a of the crystal as the rotation axis gave a clear, well-spread spectrum when the magnetic field is parallel to the c axis of the crystal. This has been identified as the x-axis of the complex which has its z and y axes in the ab plane.

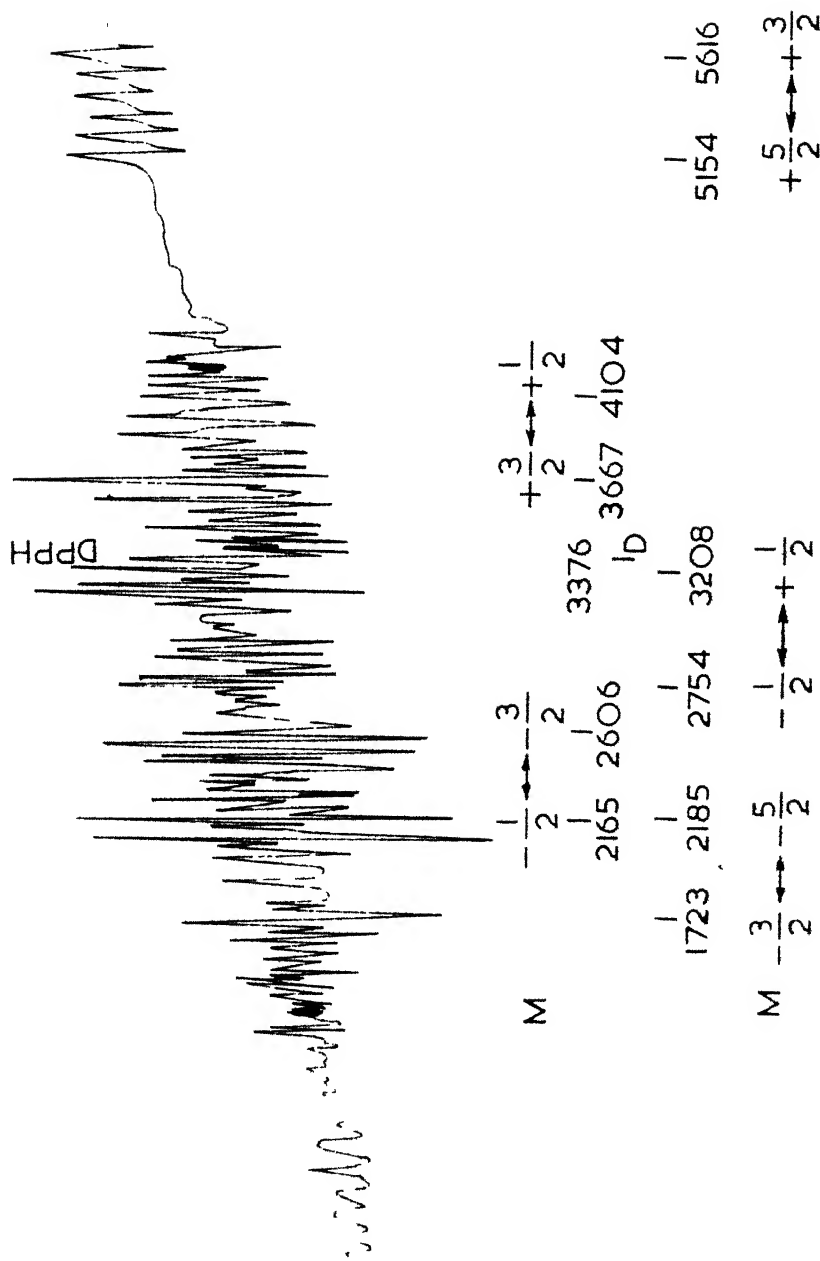


FIG.3.3 EPR SPECTRUM OF  $Mn^{2+}:Cs_2SO_4$  SINGLE CRYSTAL AT ROOM TEMPERATURE. (20°C) THE DIRECTION OF MAGNETIC FIELD IS 65° TO THE b-AXIS OF THE CRYSTAL IN THE  $ab$  PLANE  $H \parallel$  TO Y-AXIS. DPPH IS THE FIELD MARKER. NUMBERS INDICATE FIELD VALUES IN OERSTED.

DPPH

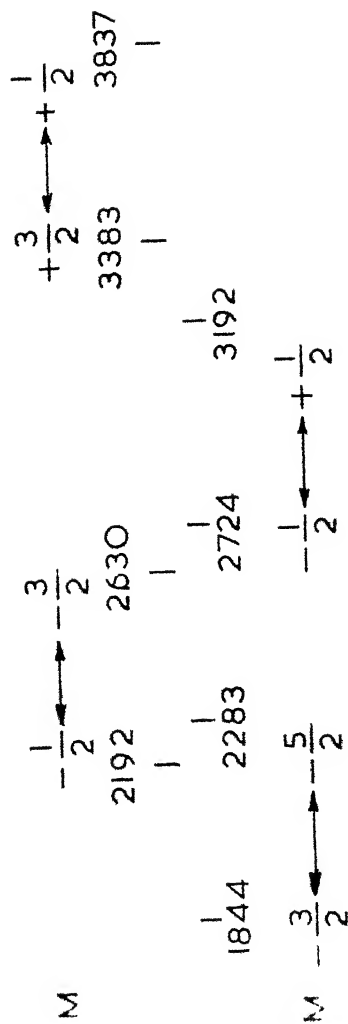


FIG.3.4 EPR SPECTRUM OF  $Mn^{2+}$  IN  $Cs_2SO_4$  SINGLE CRYSTAL AT ROOM TEMPERATURE ( $20^\circ C$ ). THE DIRECTION OF MAGNETIC FIELD IS PARALLEL TO THE C - AXIS OF THE CRYSTAL IN THE QC PLANE. H// TO X-AXIS. NUMBERS INDICATE FIELD VALUES IN OERSTED

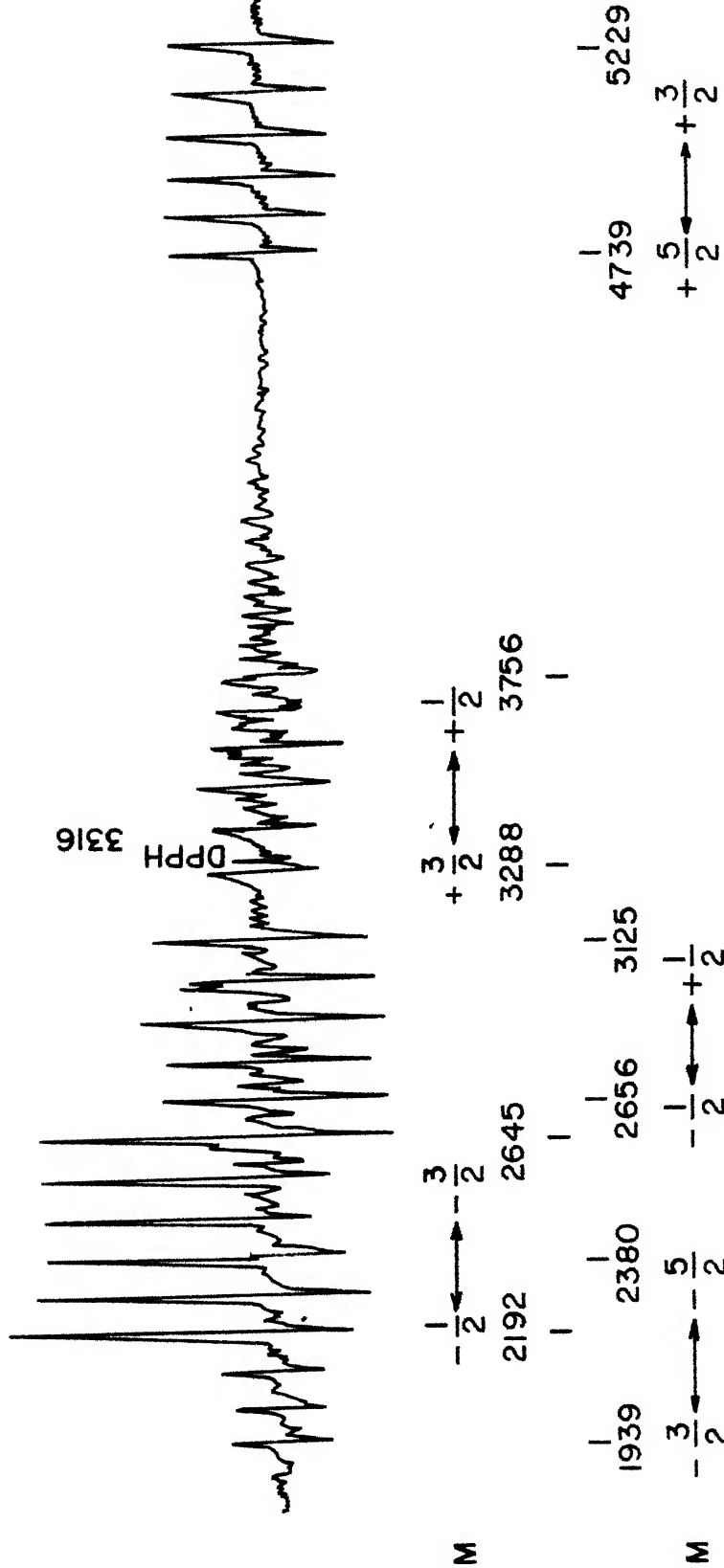


FIG. 3.6. EPR SPECTRUM OF  $Mn^{2+}$  IN  $Cs_2SO_4$  SINGLE CRYSTAL AT 77 °K. THE DIRECTION OF MAGNETIC FIELD IS PARALLEL TO THE C-AXIS OF THE CRYSTAL IN bc PLANE.

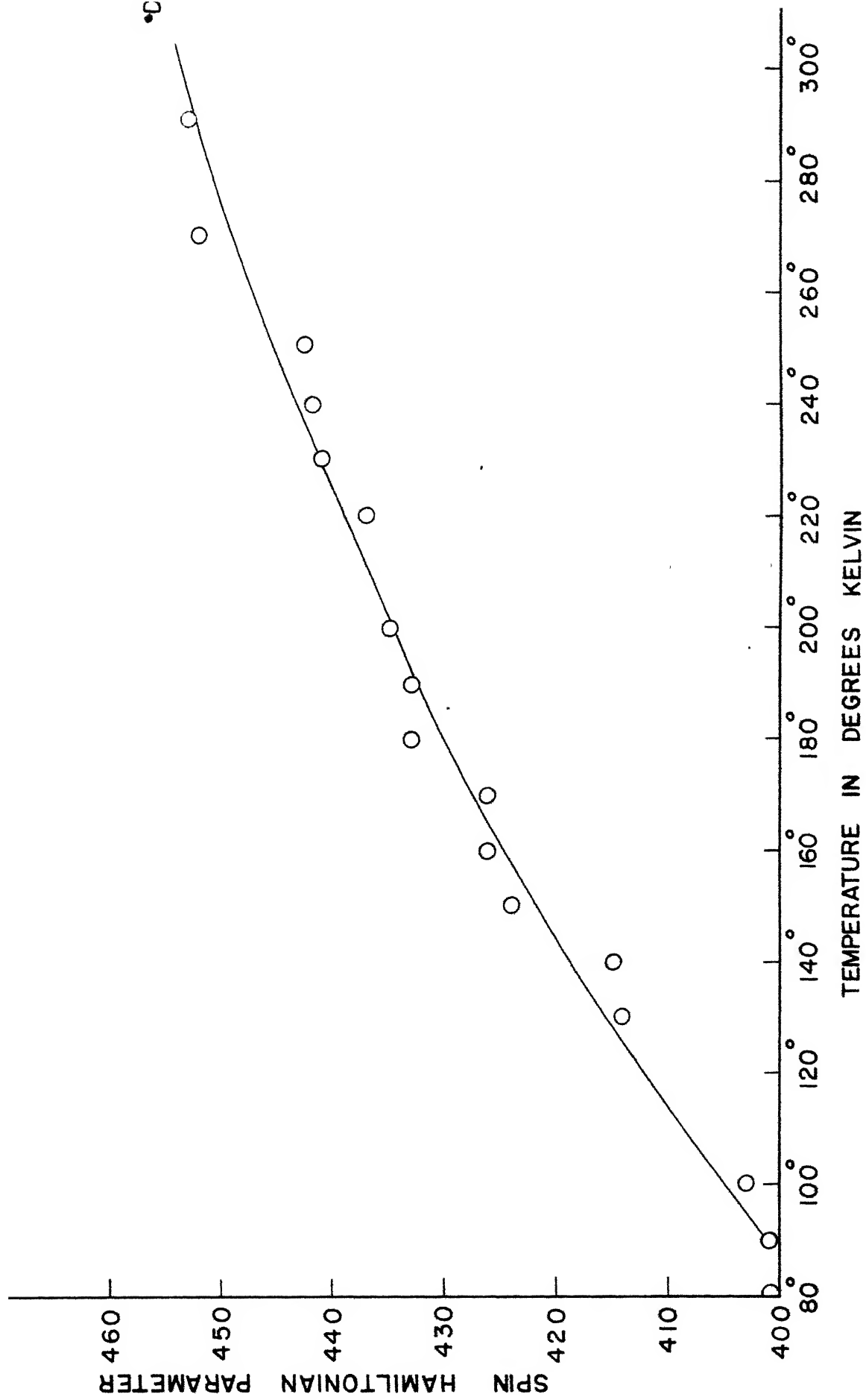


FIG.3.7 .TEMPERATURE VARIATION OF SPIN HAMILTONIAN PARAMETERS D AND E IN THE RANGE 300° K TO 77° K FOR THE  $\text{Cs}_2\text{SO}_4:\text{Mn}^{2+}$  SINGLE CRYSTAL FOR THE OBSERVED  $\beta_1$

strains which may tilt the paramagnetic axis as found by Bronstein and Maniv<sup>17</sup> in melt-grown crystals.

### 3.6 ANALYSIS OF THE SPECTRA

All the three spectra of the complex with  $H \parallel z$ ,  $H \parallel y$  and  $H \parallel x$  axes have been analysed at room temperature by the spin-Hamiltonian method. One of these with  $H \parallel x$  axis has been further analysed at  $10^\circ$  intervals between  $77^\circ\text{K}$  and  $300^\circ\text{K}$  and the spin-Hamiltonian parameters have been determined at various temperatures within this range.

The procedure which has been adopted for analysis is as follows: the three spectra relevant to the complex are examined. By inspection the M-values are assigned to each of the well-defined sextets. Assuming A's to be negative<sup>18</sup>, the relative sign of D and the sequence of M and m are determined by comparing the separation between the extreme hyperfine components of fine structure groups in high and low fields<sup>19</sup>. In the present case D is found to be negative, that is, has the same sign as A. Approximate values for the components of hyperfine tensor A, B, and C are obtained from the high field sextet specially taken with a low sweep rate of the magnetic field of about 0.4 kilooersted per minute. The first and the sixth lines of each transition fixed the position of the fine structure line. Using these fields the parameters have been found by a least square analysis with the help



of equations (3.2). Then the field values corresponding to the thirty lines have been utilised and the terms (3.2a) and (3.2b) are added to equations (3.2) and the process is repeated to get the parameters. For the spectrum which has a large effective value of  $D$ , (that is, for the spectrum with  $H \parallel z$  axis), the very low field transitions cannot be obtained with an x-band spectrometer. For this case a computer program is written for an IBM computer to diagonalise the relevant  $36 \times 36$  energy matrix. The approximate parameters obtained have been used in the usual transformation relations<sup>20</sup> to get the values of  $D^*$  and  $E^*$  which served as input parameters. They are varied until the calculated values compared favourably with the experimental values for a least-square fit. Thus to avoid inaccuracies inherent in second order perturbation formulae and to get the probable low-field values at x-band frequencies the  $D$  parameter obtained by diagonalising the energy matrix corresponding to the largest spread spectrum has been taken to be correct. For the value of  $E$  the effective values of  $D^*$  as obtained by the x and y axes spectra are taken as guide lines. The effective  $E^*$  values of the x and y axes together with  $D^*$  values serve to fix the parameters  $D$  and  $E$  ultimately. This is particularly necessary as small variations in  $E$  have great influence on the parameters obtained in x and y directions. In principle it is

possible to minimise the parameters to get the agreement between the observed and the calculated values by utilising the relations (3.2) to within 10 oersted which is the order of line width in the present case. The minimised value of  $H_0$  is utilised for calculating the corresponding g-value of the spectrum. However, to obtain the correlation among the spectra taken along the three axes z, x, and y as determined by the transformation relations<sup>20</sup> given in Table (3.1), values of the parameters which are slightly different from the minimised values are taken (at the risk of increasing the standard deviation between the experimental and calculated values). This procedure served as an additional check on the preliminary assignments made and enabled to sort out the lines in question from the angular parts. This method is a sophisticated version of that followed by Bronstein and Maniv<sup>17</sup> who tried different assignments of the transitions to obtain the expected relation between the parameters  $D^*$  and  $E^*$  in the spin-Hamiltonian. Table (3.3) gives the observed and calculated fields at resonance for the fine structure positions only while tables (3.4), (3.5), and (3.6) give the observed and calculated fields at resonance for the entire spectrum of thirty lines for the three spectra with the input parameters as indicated in each case. The main analysis of the observed complex is contained in these tables. Table (3.7) gives

TABLE 3.3

Influence of the Parameters  $b_4^0$  and  $b_4^2$   
on Resonant Field Values (Fine Structure)\*

Designation	With $b_4^0$ and $b_4^2$					Without $b_4^0$ and $b_4^2$		
	Experimental Oe	Calculated Oe	$b_4^0$ Oe	$b_4^2$ Oe	Standard deviation	Experimental Oe	Calculated	Standard deviation
Spec- trum z D=-941 E=-14 H <sub>o</sub> = 3383 Oe g <sub>z</sub> = 1.9995	7138 5275 3367 1521 -383	7147 5264 3384 1503 -383	0	13	13	7138 5275 3367 1521 -383	7147 5264 3384 1503 -383	13
Spec- trum y D*=496 E*=-461 H <sub>o</sub> *= 3366 Oe g <sub>y</sub> = 2.0096	1954 2386 2982 3886 5385	1923 2357 3001 3876 5394	-18	7	22	1954 2386 2982 3886 5385	1854 2448 2996 3787 5469	78
Spec- trum x D*=452 E*=475 H <sub>o</sub> *= 3357 Oe g <sub>x</sub> = 2.0149	2064 2411 2958 3610 5258	2039 2431 2955 3648 5247	-8	-45	23	2064 2411 2958 3610 5258	2026 2481 2917 3617 5298	44

\* Least square fit using Equations 3.2(a).

TABLE 3.4

The Lines of  $Mn^{2+}:Cs_2SO_4$  at Room Temperature 20 °CH || z-axis of the complex  
(All values in Oersted)

DPPH <sup>a</sup> 3376											
Line	+5/2 ↔ +3/2	+3/2 ↔ +1/2	+1/2 ↔ -1/2	-1/2 ↔ -3/2	-3/2 ↔ -5/2						
Observed	Ob- serv- ed	Ob- serv- ed	Ob- serv- ed	Ob- serv- ed	Ob- serv- ed						
Calculated	cal- culat- ed	cal- culat- ed	cal- culat- ed	cal- culat- ed	cal- culat- ed						
	-612	1272	1271	3136	3150	5035	5032	6899	6914		
X											
X	-520	1384	1384	3230	3243	5137	5125	7019	7007		
X	-427	1478	1456	3325	3336	5231	5218	7104	7100		
X	-334	1563	1549	3410	3429	5317	5311	7189	7193		
X	-241	1666	1642	3496	3523	5419	5404	7292	7286		
X	-148	1769	1735	3598	3616	5514	5497	7377	7379		

X Not observed at x-band; <sup>a</sup>Diphenylpicrylhydrazyl Standard deviation 16

Input parameters (for 36x36 Energy Matrix):

 $A_z(\equiv A) = -93$        $A_x(\equiv B) = -91$        $A_y(\equiv C) = -91$  $H_{oz} = 3383$  ( $g_z = 1.9995$ );  $D = -941$ ;  $E = -14$ ;  $b_1^c = 0$ ;  $b_4^c = 13$ ;  $b_4^4 = -77$

TABLE 3.5

The Lines of  $Mn^{2+}:Cs_2SO_4$  at Room Temperature 20 °C

H || y-axis of the complex  
(All values in Oersted)

DPPH<sup>a</sup> 3376

Line	-3/2 ↔ -5/2	-1/2 ↔ -3/2	-1/2 ↔ +1/2	+1/2 ↔ +3/2	+3/2 ↔ +5/2
	Ob- cal- serv- culat- ed ed	Ob- cal- serv- culat- ed ed	Ob- cal- serv- culat- ed ed	Ob- cal- serv- culat- ed ed	Ob- cal- serv- culat- ed ed
1723	1703	2165	2129	2754	2771
1819	1784	2258	2213	2846	2857
1920	1867	2350	2299	2932	2946
2025	1953	2446	2387	3024	3077
2093	2042	2555	2478	3116	3130
2185	2133	2606	2572	3208	3226
				4104	4107
				5154	5152
				5246	5243
				5338	5337
				5430	5433
				5512	5531
				5616	5633

Standard deviation 34 <sup>a</sup>Diphenylpicrylhydrazyl

Input parameters (for second order perturbation equations 3.2(a)):

$A_y(\equiv C) = -91$ ;  $A_z(\equiv A) = -93$ ;  $A_x(\equiv B) = -91$

$H_{0y} = 3366$  (g<sub>y</sub> = 2.00955);  $D_y = 496.5$ ;  $E_y = -461$ ;  $(b_4^0)_y = -18$ ;  $(b_4^2)_y = 7$

the values of the parameters obtained at 77 °K.

### 3.7 SUMMARY

The paramagnetic resonance of divalent manganese doped in caesium sulphate single crystals has been studied. A complex has been identified and a vacancy complex model has been proposed. The spectra have been obtained and analysed in all the three principal directions of g-tensor at room temperature, ( $\sim 20^\circ\text{C}$ ). One of the spectra is also analysed at liquid nitrogen temperature. In this temperature range of approximately  $220^\circ$  the rhombic field parameter  $(E^*)_x$  has decreased from 487 oersted to 470 oersted and the axial field parameter  $(D^*)_x$  has decreased from 453 oersted to 401 oersted as the temperature is lowered. The variations are smooth and no detectable changes in the spectral features occurred to suggest a phase transformation of either kind as has been indicated in the case of isomorphous  $\text{K}_2\text{SO}_4$  crystals<sup>3</sup>.

The spin-Hamiltonian parameters with deviations as suggested by correlating those obtained from transformed site axes are summarised in Table (3.8). The spectrum is broadly insensitive to the parameter  $b_4^4$  and as such its value is chosen to have consistency in the transformed parameters  $b_4^{2*}$  and  $b_4^{0*}$ .

TABLE 3.8

Spin Hamiltonian Parameters  
for  $\text{Mn}^{2+}$  in  $\text{Cs}_2\text{SO}_4$  at Room Temperature

Parameter	Value
$g_z$	$2.000 \pm 0.003$
$g_x$	$2.015 \pm 0.003$
$g_y$	$2.000 \pm 0.003$
$A_z (\equiv A)^a$	$93 \pm 1 \text{ Oe}$
$A_x (\equiv B)$	$91 \pm 1 \text{ Oe}$
$A_y (\equiv C)$	$91 \pm 1 \text{ Oe}$
$D^b$	$941 \pm 7 \text{ Oe}$
$E$	$14 \pm 3 \text{ Oe}$
$b_4^0 (\text{or } a/2)$	$0 \pm 1 \text{ Oe}$
$b_4^2$	$13 \pm 1 \text{ Oe}$
$b_4^4$	$-77 \text{ Oe}$
$\phi^c$	$25^\circ \pm 1^\circ$

- (a) A's are assumed to be negative  
 (b) The sign of D is relative to A  
 (c) The angle between the direction of the complex taken as z axis and the longest crystallographic axis.

3.8 General comments on the consistency of the spin-Hamiltonian parameters obtained from the  $H \parallel z$ ,  $H \parallel y$  and  $H \parallel x$  spectra

The parameters  $D, E, b_4^0, b_4^2$  and  $b_4^4$  given in Table (3.8) are those obtained from the analysis of the spectrum taken with  $H \parallel z$  axis of the complex. The effective values of these parameters in the  $x$  and  $y$  directions have been obtained from the analysis of the spectra with  $H \parallel y$  and  $H \parallel x$  axes and are listed in Tables (3.5) and (3.6). Expressions showing the relationships between the effective values of the parameters  $D, E, b_4^0, b_4^2$  and  $b_4^4$  along the  $z, x$ , and  $y$  directions are given in Table (3.1). The first column in Table (3.9) shows the effective values of the parameters along the  $z$  direction which are the same as those given in Table (3.4) and also in Table (3.8) and designated  $D, E, b_4^0, b_4^2$  and  $b_4^4$ . Column 2 in Table (3.9) shows these parameters calculated using the effective values obtained from the analysis of the spectrum with  $H \parallel x$  along with the necessary relations given in Table (3.1). Similarly column 3 of Table (3.9) shows the parameters derived using the constants obtained from the analysis of the spectrum with  $H \parallel y$  along with the necessary relations given in Table (3.1). The values of the parameters  $D$  are consistent within  $\pm 2.5$  oersted while those of  $E$  are consistent within  $\pm 4$  oersted. The magnitude of these deviations can probably be taken as the error



in the determination of the values of the parameters D and E. It is satisfactory to see that these deviations are not large. However, the inconsistencies or deviations can probably be reduced by using expressions involving higher orders of perturbation than used here as the term D in general and the effective values of the term E in the y and z directions have large magnitudes.

As pointed out earlier the parameter obtained from the analysis of the spectrum with  $H \parallel z$  are probably taken to be more accurate than those obtained from the other two spectra as the higher order terms in E are the least effective when H is parallel to the z axis of the complex.

It is interesting to note, though alarming in a way, that the deviations in the values of the parameters  $b_4^0$  and  $b_4^2$  in the columns 2,3 and 4 of table (3.9) are as large as the magnitude of their values. This raises a question about the usefulness of keeping these parameters in the present analysis. Table (3.3) shows the magnetic resonance field values (fine structure) calculated with and without the parameters  $b_4^0$  and  $b_4^2$ . The observed values are also included in the table for comparison and it can be seen that the standard deviation decreases to some extent when the parameters  $b_4^0$  and  $b_4^2$  are included in the analysis.

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## CHAPTER IV

### ELECTRON PARAMAGNETIC RESONANCE STUDIES OF $\text{VO}^{2+}$ IN SINGLE CRYSTALS OF CAESIUM SULPHATE †

† A preliminary account of the work was reported at the Nuclear Physics and Solid State Physics Symposium held at I.I.T., Powai, Bombay during December 1968.

## ABSTRACT

The electron paramagnetic resonance of  $\text{VO}^{2+}$  doped in caesium sulphate single crystals has been studied in three crystallographic planes. The spectrum obtained is somewhat complicated. A tentative analysis of the spectrum suggests that the  $\text{VO}^{2+}$  ions substitute the  $\text{Al}-\text{Cs}^+$  ions. The V-O bond has been found to have three preferential directions: one along the c-axis of the crystal, one in a direction making an angle of  $30^\circ$  with the c-axis in the bc plane and yet another making an angle of  $9^\circ$  with the a-axis in the ab-plane. These directions are the directions of nearest approach from the position of  $\text{Al}-\text{Cs}^+$  to the neighbouring oxygens. Optical absorption studies confirm the formation and existence of  $\text{VO}^{2+}$  ion in the crystal.

magnetic field  $H$ . The units of  $H, H_0, K, A, B$  and  $C$  are in gauss or oersted. The  $A, B$  and  $C$  of equation 4.1 are obtained by dividing those of the Hamiltonian by  $g\beta$ .

The EPR spectrum taken at any general orientation furnishes the effective  $g$ -value,  $g_{\text{eff}}$ . The square of the  $g$ -value can be expressed as<sup>12</sup>

$$g^2 = \sum_{i,j=1}^3 \tilde{A}_{ij} l_i l_j \quad (A_{ij} = A_{ji}) \quad \dots \quad (4.2)$$

So, for the general case of canted axes, the principal values of  $\underline{\tilde{g}}$  and  $\underline{\tilde{A}}$  tensors can be determined by measuring  $g_{\text{eff}}$  at several angles  $\theta$  in the three principal crystallographic planes<sup>13,14</sup>. If  $\phi_x$  is the angle made by  $H$  with the crystallographic  $y$ -axis when the plane of rotation is the  $yz$  plane, and if  $\phi_y, \phi_z$  represent the analogous angles for the rotations respectively in  $zx$  and  $xy$  planes, we have,

$yz$  plane:

$$g_{\text{eff}}^2 = (\underline{g}^2)_{yy} \cos^2 \phi_x + (\underline{g}^2)_{zz} \sin^2 \phi_x \\ + 2(\underline{g}^2)_{yz} \cos \phi_x \sin \phi_x$$

$zx$  plane:

$$g_{\text{eff}}^2 = (\underline{g}^2)_{zz} \cos^2 \phi_y + (\underline{g}^2)_{xx} \sin^2 \phi_y \\ + 2(\underline{g}^2)_{zx} \cos \phi_y \sin \phi_y$$

xy plane:

$$g_{\text{eff}}^2 = (g^2)_{xx} \cos^2 \phi_z + (g^2)_{yy} \sin^2 \phi_z + 2(g^2)_{xy} \cos \phi_z \sin \phi_z \quad \dots \quad (4.3)$$

Here  $(g^2)_{ij}$ ,  $i$  and  $j$  taking values from 1 to 3, are the elements of the  $g^2$ -tensor. The principal  $g$ -values are found by diagonalising the matrix  $\tilde{A}$ , (not given explicitly, equation 4.2), which is formed using the relations (4.3) or the equivalent form

$$g^2 = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta \quad \dots \quad (4.4)$$

where  $\alpha$ ,  $\beta$  and  $\gamma$  are found by a least-square fit of the experimental data. The sign of the off-diagonal elements is to be determined from a  $g^2$ - $\theta$  plot and noting the position of maxima and minima with respect to the reference axes.

#### 4.3 . EXPERIMENTAL PROCEDURE

Single crystals of caesium sulphate containing small concentration of vanadyl ion are grown by slow evaporation of aqueous solution of caesium sulphate of E. Merck, analar quality, with an initial concentration of 0.5 mol percent of vanadyl sulphate. Well developed, rectangular, boat-shaped crystals have been obtained the sizes varying from one centimeter to a few millimeters in length. Spectrophotometric analysis of the experimental

crystal yielded 300 ppm of vanadium. Optical absorption measurements were done on a Cary-14 spectrophotometer. The remaining experimental details are the same as those discussed in chapter III.

#### 4.4 RESULTS AND DISCUSSION

The structure of caesium sulphate with the metal oxygen directions marked in the bc and ac planes is shown in Figs. 4.1(a) and 4.2(b) respectively. The positional coordinates of the atoms are listed by Ogg.<sup>15</sup> The  $\text{Cs}^+$  ions and two of the oxygens of the sulphate group lie in the bc plane. Depending upon the oxygen environment the  $\text{Cs}^+$  ions are divided<sup>15</sup> into two types  $\alpha$  and  $\beta$ . Considering an  $\alpha$ - $\text{Cs}^+$  ion, there is an oxygen atom along the c-axis at a distance of 3.1 Å. Another oxygen atom is at an angle of  $27^\circ 36'$  to the c-axis in the bc plane and is at a distance of 3.28 Å. A third oxygen atom is at an angle of  $7^\circ 36'$  to the a-axis in the ab-plane and is at a distance of 3.2 Å. These three oxygen atoms are designated in this work as I, II and III respectively, Fig.(4.1).

Angular variation of the EPR spectra of  $\text{VO}^{2+}$  in  $\text{Cs}_2\text{SO}_4$  is carried out in the three crystallographic planes, viz., ab, bc and ca of the crystal. The spectra obtained in different important directions are shown in Figures 4.2 — 4.6. Three complexes which are magnetically inequivalent are found to exist. The spectrum of complex I



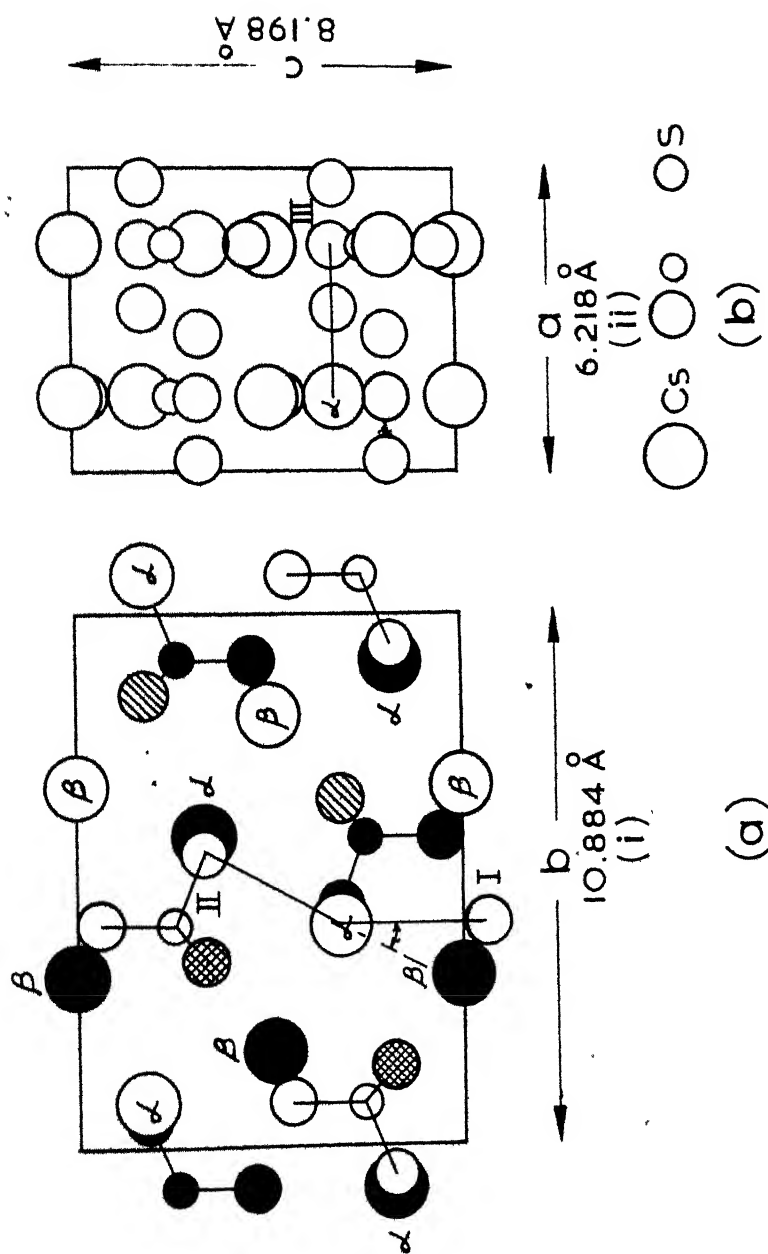


FIG. 4.1—PROJECTION OF ATOMS OF CAESIUM SULPHATE CRYSTAL IN  $bc$  AND  $ac$  PLANES

$\text{Cs}\alpha - \text{O}_I$  COMPLEX I ALONG THE  $c$ -AXIS

$\text{Cs}\alpha - \text{O}_{II}$  COMPLEX II AT ANGLE OF  $30^\circ$  TO  $c$ -AXIS

$\text{Cs}\alpha - \text{O}_{III}$  COMPLEX III ALONG  $a$ -AXIS

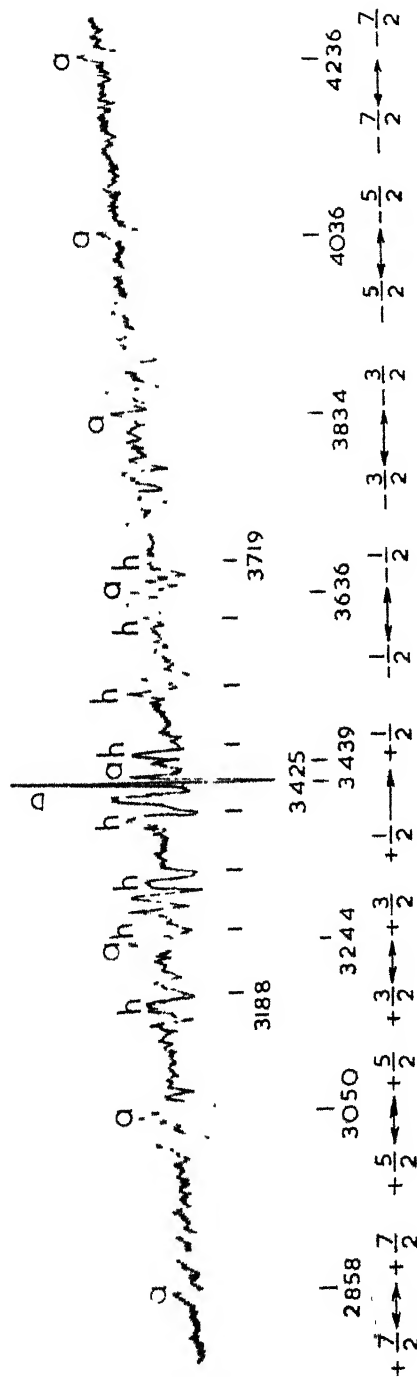


FIG. 4.2 EPR SPECTRUM OF  $\text{VO}^{2+}$  IN  $\text{CS}_2\text{SO}_4$  SINGLE CRYSTAL AT ROOM TEMPERATURE.  
 $\text{H} \parallel \text{C}$  (b-AXIS VERTICAL) a's REFER TO  $I_z$ , h's REFER TO  $\text{H}_x$ ; D IS THE FIELD  
 MARKER FIELD VALUES IN OERSTED.

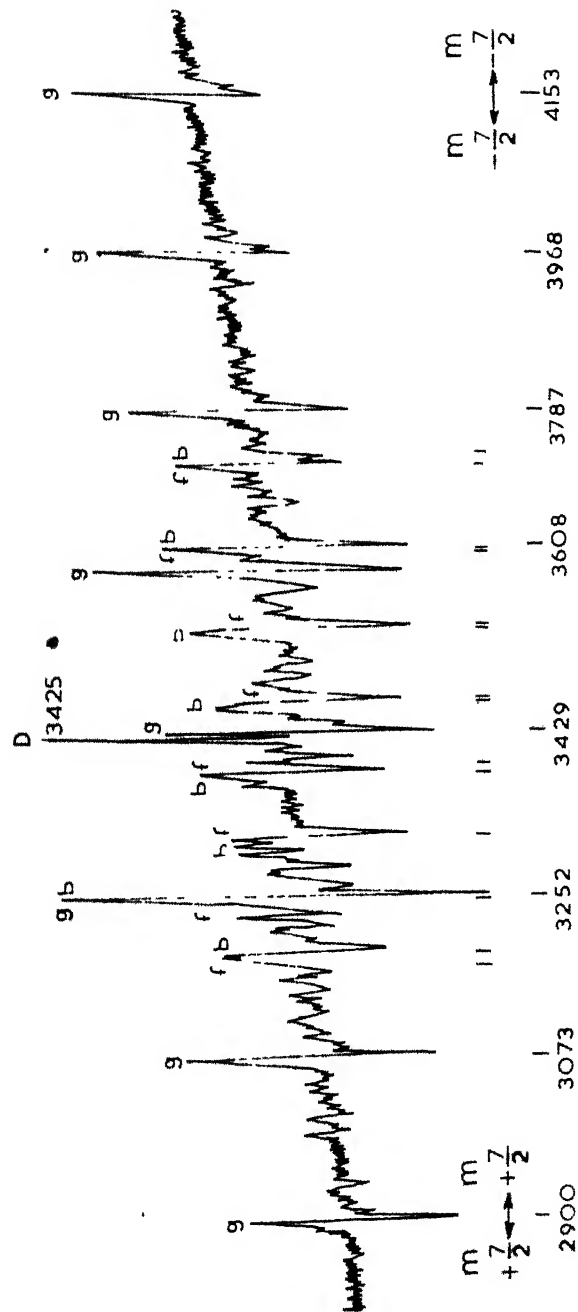


FIG. 4.3 EPR SPECTRUM OF  $\text{VO}^{2+}$  IN  $\text{CS}_2\text{SO}_4$  SINGLE CRYSTAL AT ROOM TEMPERATURE  $\text{H} \parallel \text{a}$  AXIS (b-AXIS VERTICAL) g's DENOTE VO III Z-AXIS, b's DENOTE VO I X-AXIS, f's DENOTE VO II Y-AXIS, D IS THE FIELD MARKER ALL VALUES ARE IN GAUSS.

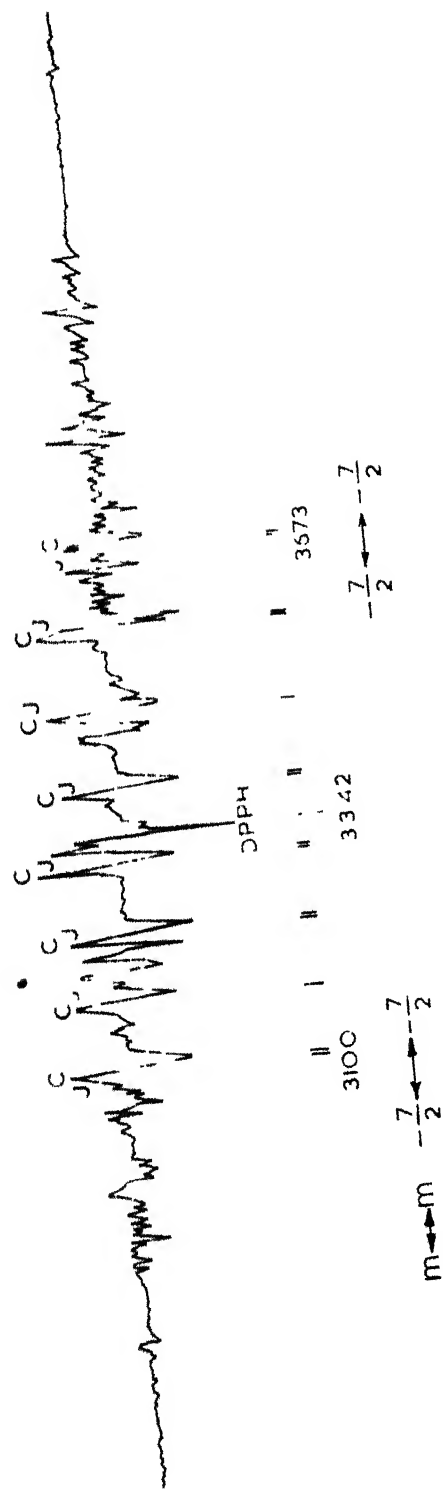


FIG.4.4 EPR SPECTRUM OF  $\text{VO}_2^+$  IN  $\text{Cs}_2\text{SO}_4$  SINGLE CRYSTAL AT ROOM TEMPERATURE.  $H \parallel b$ -AXIS (a-AXIS VERTICAL) C'S DENOTE  $I_Y$ , J'S DENOTE  $I_X$ , DPPH IS THE FIELD MARKER, FIELD VALUES ARE IN OERSTED.

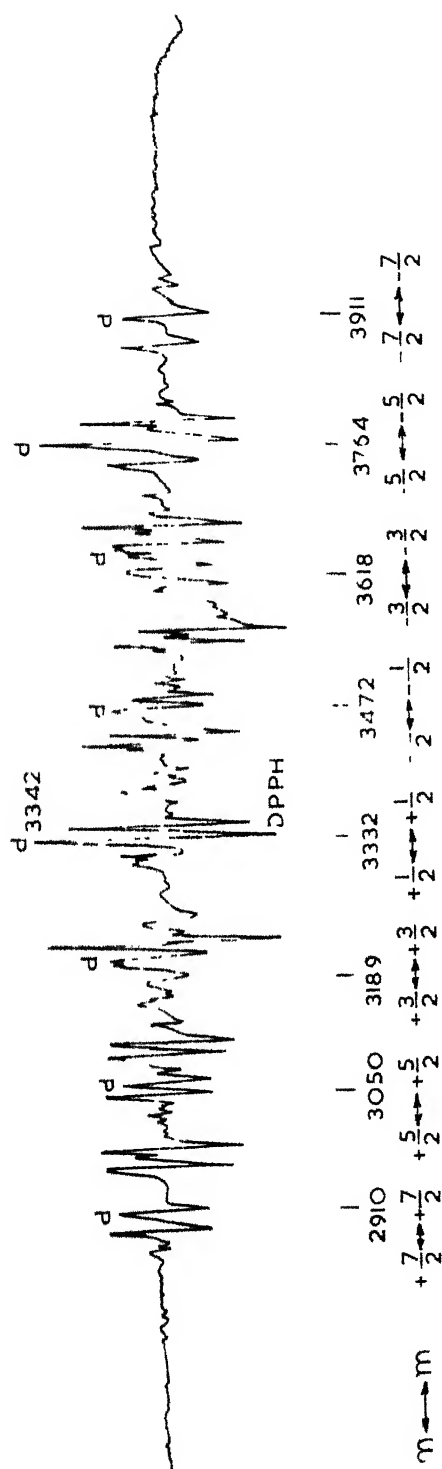


FIG. 4.5 EPR SPECTRUM OF  $\text{VO}^{2+}$  IN  $\text{CS}_2\text{SO}_4$  SINGLE CRYSTAL AT ROOM TEMPERATURE. H AT AN ANGLE OF  $30^\circ$  TO C-AXIS (C-AXIS VERTICAL)  $d$ 'S DENOTE  $\text{II}_Z$ , DPPH IS THE FIELD MARKER FIELD VALUES ARE IN OERSTED

and their direction cosines have been determined by adopting the procedure outlined briefly in section 4.2. The angle which the principal  $z$  axis of the  $g$  tensor makes with the crystallographic  $a$  axis in the  $ab$  plane comes out to be  $9^{\circ}6'$  as compared to  $7^{\circ}36'$  calculated from the structural parameters<sup>15</sup>. The acute angles which the other principal components ( $x$  and  $y$ ) of the  $g$ -tensor make respectively with the crystallographic  $b$  and  $c$  axes are found to be  $9^{\circ}6'$  and  $8^{\circ}42'$ .

The angular variations of the spectral lines in complexes I, II and III indicate that the principal axes of the  $g$  and  $A$  tensors coincide in all the complexes.

The  $z$  directions of the complexes I, II and III nearly coincide with the directions of nearest approach from the position of  $\alpha$ -Cs<sup>+</sup> to three neighbouring oxygens marked I, II and III in Fig.4.1 and referred to in the earlier part of the chapter. This suggests that the VO<sup>2+</sup> substitutes the  $\alpha$ -Cs<sup>+</sup> ions and the VO-bonds of the complexes are along the  $z$  directions of the respective complexes.

The observed and the calculated magnetic field resonance values are given in Tables 4.1 to 4.3. Calculations for the least square fit are done with the help of an IBM 1620 computer. The spin-Hamiltonian parameters obtained for the different complexes are included in the Tables 4.1 to 4.3 at the appropriate places.

TABLE 4.1

Observed and Calculated Field Values  
of the Spectrum I

(Result of the least-square fit)  
Field values in Oersted

Transition $m \leftrightarrow m$	Spectrum I <sub>z</sub> H    c		Spectrum I <sub>x</sub> H    a		Spectrum I <sub>y</sub> H    b	
	Fig. 4.3 a's		Fig. 4.4 b's		Fig. 4.5 c's	
	Observ- ed	Calcu- lated	Observ- ed	Calcu- lated	Observ- ed	Calcu- lated
+7/2 ↔ +7/2	2858	2859	3195	3194	3100	3100
+5/2 ↔ +5/2	3050	3050	3252	3252	3161	3162
+3/2 ↔ +3/2	3244	3244	3318	3316	3228	3230
+1/2 ↔ +1/2	3439	3439	3385	3387	3303	3305
-1/2 ↔ -1/2	3636	3636	3465	3465	3387	3386
-3/2 ↔ -3/2	3834	3835	3547	3549	3476	3474
-5/2 ↔ -5/2	4036	4035	3640	3640	3568	3569
-7/2 ↔ -7/2	4236	4238	3737	3737	3673	3671
	Standard Deviation $\Delta = 1.2$ $A_z (\equiv A) = 197$ Oe $H_{oz} = 3540.5$ Oe $g_z = 1.9382$		Standard Deviation $\Delta = 1.2$ $A_x (\equiv B) = 77.50$ e $H_{ox} = 3437.5$ Oe $g_x = 1.9963$		Standard Deviation $\Delta = 1.4$ $A_y (\equiv C) = 81.5$ Oe $H_{oy} = 3357.0$ Oe $g_y = 1.9947$	

TABLE 4.2

Observed and Calculated Field Values  
of the Spectrum II  
(Result of the least-square fit)  
Field values in Oersted

Transition $m \leftrightarrow m$	Spectrum II <sub>z</sub> H in bc plane 30° to c		Spectrum II <sub>x</sub> H in bc plane 120° to c		Spectrum II <sub>y</sub> H    a	
	Fig. 4.6 d's		Fig. 4.7 e's		Fig. 4.4 f's	
	Observ-	Calcu-	Observ-	Calcu-	Observ-	Calcu-
	ed	lated	ed	lated	ed	lated
+7/2 ↔	2910	2910	3138	3137	3183	3182
+7/2						
+5/2 ↔	3050	3049	3192	3191	3248	3248
+5/2						
+3/2 ↔	3189	3189	3249	3248	3318	3319
+3/2						
+1/2 ↔	3332	3330	3309	3310	3393	3392
+1/2						
-1/2 ↔	3472	3473	3377	3375	3470	3470
-1/2						
-3/2 ↔	3618	3618	3444	3445	3551	3551
-3/2						
-5/2 ↔	3764	3764	3517	3518	3636	3636
-5/2						
-7/2 ↔	3911	3911	3596	3595	3724	3724
-7/2						
	Standard Deviation $\Delta = 0.9$ $A_z (\equiv A) = 143$ Oe $H_{oz} = 3404.5$ Oe $g_z = 1.9669$		Standard Deviation $\Delta = 1.0$ $A_x (\equiv B) = 65.5$ Oe $H_{ox} = 3349.5$ Oe $g_x = 1.9992$		Standard Deviation $\Delta = 0.6$ $A_y (\equiv C) = 77.5$ Oe $H_{oy} = 3437.5$ Oe $g_y = 1.9963$	



TABLE 4.3

Observed and Calculated Field Values  
of the Spectrum III  
(Result of the least-square fit)  
Field values in Oersted

Transition $m \leftrightarrow m$	Spectrum III <sub>z</sub> H    a		Spectrum III <sub>x</sub> H    c		Spectrum III <sub>y</sub> H    b	
	Fig. 4.4 g's		Fig. 4.3 h's		Fig. 4.5 j's	
	Observ-	Calcu-	Observ-	Calcu-	Observ-	Calcu-
	ed	lated	ed	lated	ed	lated
+7/2 $\leftrightarrow$	2900	2901	3188	3188	3096	3095
+7/2 $\leftrightarrow$						
+5/2 $\leftrightarrow$	3073	3074	3246	3247	3161	3161
+5/2 $\leftrightarrow$						
+3/2 $\leftrightarrow$	3252	3250	3312	3312	3232	3231
+3/2 $\leftrightarrow$						
+1/2 $\leftrightarrow$	3429	3427	3383	3382	3307	3308
+1/2 $\leftrightarrow$						
-1/2 $\leftrightarrow$	3608	3606	3459	3458	3391	3390
-1/2 $\leftrightarrow$						
-3/2 $\leftrightarrow$	3787	3787	3540	3540	3476	3477
-3/2 $\leftrightarrow$						
-5/2 $\leftrightarrow$	3968	3969	3627	3627	3572	3571
-5/2 $\leftrightarrow$						
-7/2 $\leftrightarrow$	4153	4154	3719	3720	3669	3669
-7/2 $\leftrightarrow$						
	Standard Deviation = 1.5 $A_z (=A) = 179 \text{ Oe}$ $H_{oz} = 3519.5 \text{ Oe}$ $g_z = 1.9498$		Standard Deviation 0.7 $A_x (=B) = 76 \text{ Oe}$ $H_{ox} = 3430 \text{ Oe}$ $g_x = 2.0006$		Standard Deviation 1.5 $A_y (=C) = 82 \text{ Oe}$ $H_{oy} = 3358.5 \text{ Oe}$ $g_y = 1.9939$	

It may be noted here that for all the complexes  $A_z$  is much larger than  $A_x$  and  $A_y$ . It is also found that the values of  $g_z$  are comparatively much smaller than the values of  $g_x$  and  $g_y$  for all the three complexes. Again, the values of  $g_x$  and  $g_y$  are nearer to one another in all the complexes, the value of  $g_x$  being slightly larger than that of  $g_y$ .

From the crystal structure data<sup>15</sup> the distances  $Cs_A - O(I)$ ,  $Cs_A - O(II)$  and  $Cs_A - O(III)$  are respectively 3.1 Å, 3.28 Å and 3.2 Å. The magnitudes of the hyperfine constants ( $A_z$ ) for the complexes I, II and III are respectively 197, 143 and 179 Oersted. The values of  $g_z - g_x$  for complexes I, II and III are respectively 0.0581, 0.0323 and 0.0508. Again, the values of  $g_z$  are 1.9382, 1.9669 and 1.9498 respectively for the complexes I, II and III. It is interesting to note that the changes in  $A_z$ , ( $g_z - g_x$ ) or ( $g_z - g_y$ ) and  $g_z$  as we go from complex I to complex III are related to the respective  $Cs_A - O(I, II, III)$  distances.

In order to confirm the formation and existence of  $VO^{2+}$  ion in the vanadyl doped  $Cs_2SO_4$  crystal, optical absorption spectrum of the crystal has been recorded. The spectrum obtained is shown in Fig.(4.7). It reveals a broad absorption band with a maximum at about 8000 Å ( $12,500\text{ cm}^{-1}$ ) along with a shoulder at about 6250 Å ( $16,000\text{ cm}^{-1}$ ). This is consistent with the spectrum that one expects for  $VO^{2+}$  ion. The  $VO^{2+}$  in vanadyl solutions

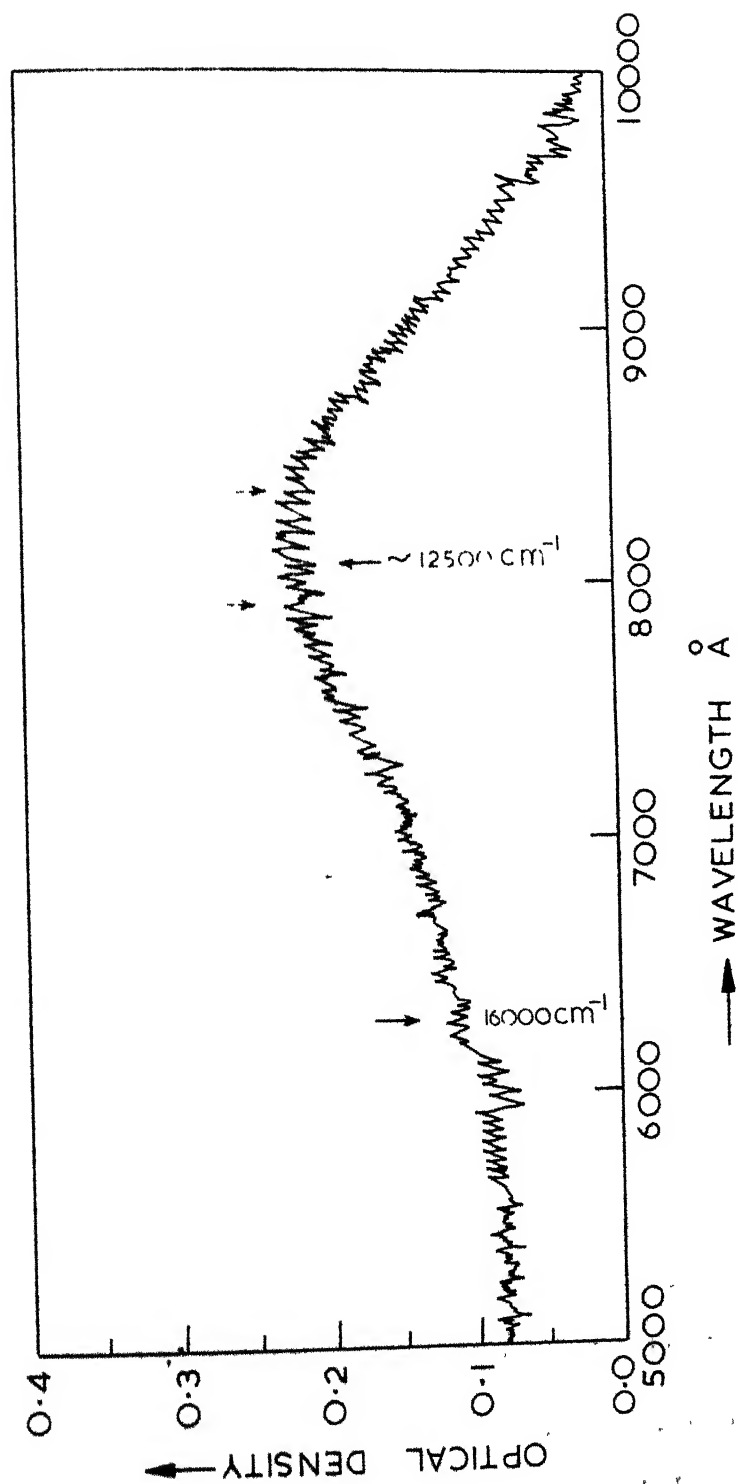


FIG.4.7 OPTICAL ABSORPTION SPECTRUM OF  $\text{VO}_2^+$  IN  $\text{CS}_2\text{SO}_4$  SINGLE CRYSTAL.

is known<sup>16</sup> to give an absorption with a maximum at 13,000  $\text{cm}^{-1}$  and a shoulder at 16,000  $\text{cm}^{-1}$ . In potassium aluminium (KAl) alum and ammonium aluminium ( $\text{NH}_4\text{Al}$ ) alum<sup>6</sup> doped with  $\text{VO}^{2+}$  absorption bands have been obtained at 13,000  $\text{cm}^{-1}$  and 15,700  $\text{cm}^{-1}$  while in methyl ammonium gallium (MAG) alum<sup>7</sup> they are at 12,700  $\text{cm}^{-1}$  and 15,200  $\text{cm}^{-1}$  respectively. The  $\text{VO}^{2+}$  is known to replace the trivalent metal ion in the alums and form  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  with the neighbouring water molecules. Thus  $\text{VO}^{2+}$  in these crystals appears to have a distorted octahedral coordination. The two absorption bands of  $\text{VO}^{2+}$  in the visible region in the vanadyl solutions have been interpreted by Jorgensen<sup>17</sup> treating the molecule as a strongly tetragonally distorted octahedron  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  and by Furlani<sup>18</sup> by considering only  $C_{4v}$  point symmetry. Jorgensen interprets the spectrum of  $\text{VO}^{2+}$  in terms of an energy level diagram<sup>19</sup> shown in Fig.(4.8). The left of the figure shows the effect of an axial tetragonal component appropriate to the  $d^1$  ions while the right of the diagram shows the effect of a square tetragonal component. The observed transitions are thought to be  ${}^2B_2 \rightarrow E$  and  ${}^2B_2 \rightarrow {}^2B_1$ . According to Ballhausen<sup>16</sup> the band at 13,000  $\text{cm}^{-1}$  is due to the first transition and the one at 16,000  $\text{cm}^{-1}$  is due to the second transition.

It is difficult to visualize a tetragonally distorted octahedral coordination for the vanadyl ion at the  $\alpha \rightleftharpoons \text{Cs}^+$  site. If it is an octahedral coordination, it must

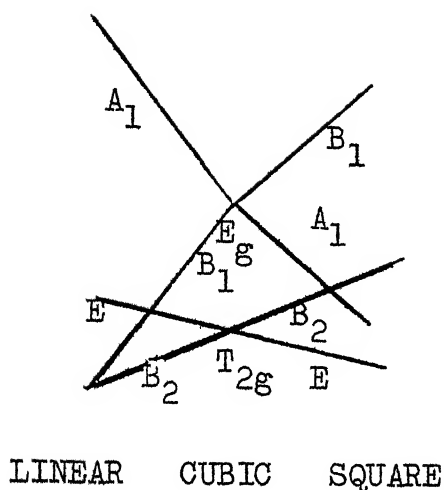


Fig.4.8. Energy levels of a single d-electron in fields of octahedral and tetragonal symmetry. The right side of the diagram applies to the case in which the polar ligands are farther away (or have a lower charge) than the equatorial ligands of the octahedron. The left side is for the opposite case. (From reference 19).

## CHAPTER V

ELECTRON PARAMAGNETIC RESONANCE OF  $Mn^{2+}$   
IN NaF SINGLE CRYSTALS\*

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\* This work has been recently published: A.V. Jagannadham and Putcha Venkateswarlu, Proc. Ind. Acad. Sci. 69, 67 (1969).

## ABSTRACT

The electron paramagnetic resonance of  $\text{Mn}^{2+}$  in NaF single crystals is investigated at different temperatures from 573 °K to 93 °K. Four different spectra designated as I, II,  $\text{III}_2$  and  $\text{III}_4$  are observed. Spectrum I consists of a single broad resonance corresponding to precipitated  $\text{Mn}^{2+}$  ions. Spectrum II is isotropic and centred near  $g=2.00$ . This spectrum corresponds to substitutional  $\text{Mn}^{2+}$  ions with remote charge compensating sites and therefore with local cubic symmetry. Spectrum  $\text{III}_2$  with  $g=2.014$  and spectrum  $\text{III}_4$  with  $g=1.995$  are also due to substitutional  $\text{Mn}^{2+}$  ions but subjected to tetragonal crystalline fields and are the same as those reported by earlier workers. Superhyperfine structure has been observed in spectra II,  $\text{III}_2$  and  $\text{III}_4$ . The analysis of that structure in spectra II and  $\text{III}_2$  has been carried out for the first time and the constants  $A_g$  and  $A_\sigma$  are given. The spectra are analysed by the usual spin-Hamiltonian method.

## 5.1 INTRODUCTION

It is known that when alkali halide crystals are doped with divalent impurities like  $\text{Mn}^{2+}$ , alkali vacancies are created to maintain charge neutrality. The divalent ions could individually go in substitutionally or interstitially in the crystal or could also go in clusters or precipitates. The vacancy could be a nearby neighbour to the divalent ion or it could be far away from it. The electron paramagnetic resonance (EPR) spectra<sup>1,7</sup> clearly indicate the different ways in which the impurity ions go into the crystals. Earlier work<sup>5,6</sup> on  $\text{Mn}^{2+}:\text{NaCl}$  has shown that the following different types of EPR spectra could be obtained depending upon the way in which the crystal is grown: (I) a broad absorption due to clusters or precipitates of  $\text{Mn}^{2+}$ , (II) a spectrum showing only one hyperfine sextet which is due to  $\text{Mn}^{2+}$  in cubic symmetry the vacancies being far away, (III<sub>1</sub>) an orthorhombic spectrum due to  $\text{Mn}^{2+}$  associated with a first neighbour alkali vacancy along the  $\langle 110 \rangle$  direction, (III<sub>2</sub>) a tetragonal spectrum due to  $\text{Mn}^{2+}$  associated with a second neighbour alkali vacancy along  $\langle 100 \rangle$ , (IV) an orthorhombic spectrum due to  $\text{Mn}^{2+}$  associated with a molecular oxygen ion in the first neighbour halogen site, and (V) a tetragonal spectrum due to  $\text{Mn}^{2+}$  associated probably with a hydroxyl ion again in the first neighbour halogen site. Hayes and Jones<sup>3</sup> investigated the EPR of  $\text{Mn}^{2+}:\text{NaF}$  and reported a strong tetragonal spectrum which is called here for convenience as III<sub>4</sub>.



and also a weak spectrum of the same kind which is designated here as  $\text{III}_2$ . Both these spectra have also been analysed. They are reported to reveal super-hyperfine structure (SHFS) though the involved constants for only the strong spectrum  $\text{III}_4$  had been obtained. In order to see whether the other types of the spectra reported for  $\text{Mn}^{2+}:\text{NaCl}$  could also be found the EPR of  $\text{Mn}^{2+}:\text{NaF}$  has been re-investigated with larger samples at different temperatures in the range  $573^\circ\text{--}93^\circ\text{K}$ . The present paper deals with the results obtained in such an investigation.

## 5.2 EXPERIMENTAL

Electron paramagnetic resonance (EPR) studies at room temperature are made with a large single crystal of NaF of an approximate volume of one cubic centimeter containing 0.1% of manganese. This crystal is cleaved from a melt-grown crystal supplied by OPTOVAC and is quite transparent. The crystal was grown in vacuum in a graphite crucible. Smaller crystals cut from the above large crystal are used for studying the spectra between  $573^\circ\text{K}$  and  $93^\circ\text{K}$ . A Varian X-band spectrometer V-4502-12 with 100 kc./sec. field modulation is used. Angular variation is studied with the sample in a V-4533 rotating cavity while the temperature studies are made with V-4547 variable temperature accessories. The magnetic field is measured with a model F-8 flux meter. The frequency of the proton resonance is measured with a Hewlett Packard

frequency counter HP-524C. The field has been standardised using a polycrystalline sample of the free radical  $\alpha$ - $\alpha'$ -diphenyl  $\beta$ -picryl hydrazyl (DPPH) as a field marker the g-value of which is taken as  $2.0036 \pm 0.0002^8$ .

### 5.3 THEORY

The  $Mn^{2+}$  spectrum has been discussed well by various authors.<sup>9-11</sup> Divalent manganese has a  $3d^5$  electron configuration for which the ground term is  $^6S_{5/2}$ . This state splits into three Kramers' doublets in the presence of an electric field having an axial or lower symmetry. This splitting gives rise to five fine structure lines in the EPR spectrum of  $Mn^{2+}$  which further split into sextets due to hyperfine interaction with the nucleus. An axial spectrum is described by a spin-Hamiltonian

$$\begin{aligned}
 H = & g \beta H_z \underline{S}_z + A^{55} \underline{S} \cdot \underline{I} + \frac{a}{6} \left[ S_x^4 + S_y^4 + S_z^4 \right. \\
 & \left. - \left( -\frac{1}{5} \right) S(S+1)(3S^2 + 3S - 1) \right] \\
 & + D \left[ S_z^2 - \left( -\frac{1}{3} \right) S(S+1) \right] \quad \dots \quad (5.1)
 \end{aligned}$$

The first term in Equation (5.1) describes the Zeeman interaction of the electron spin ( $S=5/2$ ) with the applied static magnetic field  $H$ ,  $g$  is the spectroscopic splitting factor and  $\beta$  is the Bohr magneton. The second term is due to the nuclear hyperfine interaction,  $A^{55}$  being the hyperfine interaction constant due to manganese nucleus. ' $I$ ' is the nuclear spin of manganese ( $I=5/2$ ). The third and

the fourth terms are related to the splittings of the electronic levels in the zero magnetic field due to the crystalline electric field. The crystal field parameters  $a$  and  $D$  correspond, respectively, to the cubic and tetragonal fields. In the present case a term of the type  $\sum S \cdot A_i^1 \cdot I_0^1$  is added to the spin-Hamiltonian since there exists a magnetic interaction between  $Mn^{2+}$  ion and the surrounding  $F^-$  ligand nuclei whose spin is  $I_0 (=1/2)$ . This interaction produces a shift  $\delta H$  in the field at which resonance occurs<sup>12,3</sup>

$$\delta H = \sum_i I_{0z}^1 \left\{ A_s^1 + A_\sigma^1 (3 \cos^2 \theta_{z,\sigma} - 1) \right\} \quad \dots \quad (5.2)$$

where the summation is over the six fluorine nuclei. It is assumed that the magnetic electrons are partly in  $p\sigma$  orbitals on fluorines and that the magnetic field is applied along the  $z$ -axis at an angle  $\theta_{z,\sigma}$  with the axis of each  $\sigma$  bond.  $A_s$  is the isotropic part and is determined by the  $s$  electron contact interaction.  $A_\sigma$  is the anisotropic part and it includes the dipole-dipole interaction and the coupling with the  $p\sigma$  orbitals. As the six fluorines form an octahedron around  $Mn^{2+}$ , the interaction parameters  $A_s$  and  $A_\sigma$  can be expected to be the same for all the fluorine nuclei. When the magnetic field is parallel to the crystallographic axis  $\langle 100 \rangle$ , two fluorines along the field direction will be equivalent while the four fluorines in the plane perpendicular to the field direction will be equivalent among themselves. In such

a case Equation (5.1) takes the form

$$\delta H = A_S \sum_1^6 I_{Oz}^i + 2A_O \sum_1^4 I_{Oz}^i - A_O \sum_1^4 I_{Oz}^i \quad \dots \quad (5.2a)$$

where  $I_{Oz}$  can take the values  $\frac{1}{2}$  or  $-\frac{1}{2}$ . The resulting number of lines in this case will be fifteen and the expressions for  $\delta H$  for the individual lines along with their relative intensities are given in columns 3 and 2 of Table 5.1. In practice the number of lines observed will be smaller than fifteen. This is because of the considerable line width and the overlaps will be dependent upon the relative magnitudes of  $A_S$  and  $A_O$ . If  $A_O$  is exactly equal to zero there will be seven lines all of which will be equally separated from one another.

The field values corresponding to the different transitions when the static magnetic field is parallel to the  $\langle 100 \rangle$  direction are given by<sup>5,6</sup>

$$H(M=+\frac{1}{2} \leftrightarrow -\frac{1}{2}) = H_0 \quad \dots \quad (5.3)$$

$$H(M=\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}) = H_0 \mp 2D \pm 5a/2 \quad \dots \quad (5.4)$$

$$H(M=\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}) = H_0 \mp 4D \pm 2a \quad \dots \quad (5.5)$$

to which the following expression for hyperfine structure is to be added:

$$H(m \leftrightarrow m) = -A^{55}m - A^2/2H_0 \cdot [\overline{I(I+1)-m^2} + (2M-1)\underline{m}] \quad (5.6)$$

Here  $H_0 = h\nu/g\beta$ ,  $\nu$  being the microwave frequency.

$$\text{and } A_{\sigma} = 3.3G$$

$$(M = +5/2 \rightarrow 3/2 \text{ and } m = -5/2 \rightarrow -3/2)$$

Line Nos.	Relative statistical weight	$\delta H$	$\delta H$ in gauss	$\delta H$ expected peaks in gauss	Calculated relative intensity	$H = m + 2122.0$ in gauss	$H$ observed in gauss	Observed relative intensity
1	1	$-3A_S$	-42.9	-42.9	1	2085.1	2083.9	1
2	4	$-(2A_S + A_{\sigma})$	-31.9	-31.9	4	2096.1	2097.2	5
3	2	$-2(A_S - A_{\sigma})$	-22.0	-22.0	8	2106.8	2106.9	10
4	6	$-(A_S + 2A_{\sigma})$	-20.9	-20.9	12	2117.4	2117.4	13
5	8	$-(A_S - A_{\sigma})$	-11.0	-11.0	14	2128.0	2128.8	14
6	4	$-3A_{\sigma}$	-9.9	-9.9	12	2138.6	2138.9	14
7	1	$-(A_S - 4A_{\sigma})$	-1.1	-1.1	8	2149.2	2149.0	11
8	12	0	0	0	4	2159.9	2159.4	6
9	1	$(A_S - 4A_{\sigma})$	1.1	1.1	1	2170.9	2170.1	2
10	4	$3A_{\sigma}$	9.9	9.9				
11	8	$(A_S - A_{\sigma})$	11.0	11.0				
12	6	$+(A_S + 2A_{\sigma})$	20.9	20.9				
13	2	$2(A_S - A_{\sigma})$	22.0	22.0				
14	4	$(2A_S + A_{\sigma})$	31.9	31.9				
15	1	$3A_S$	42.9	42.9				

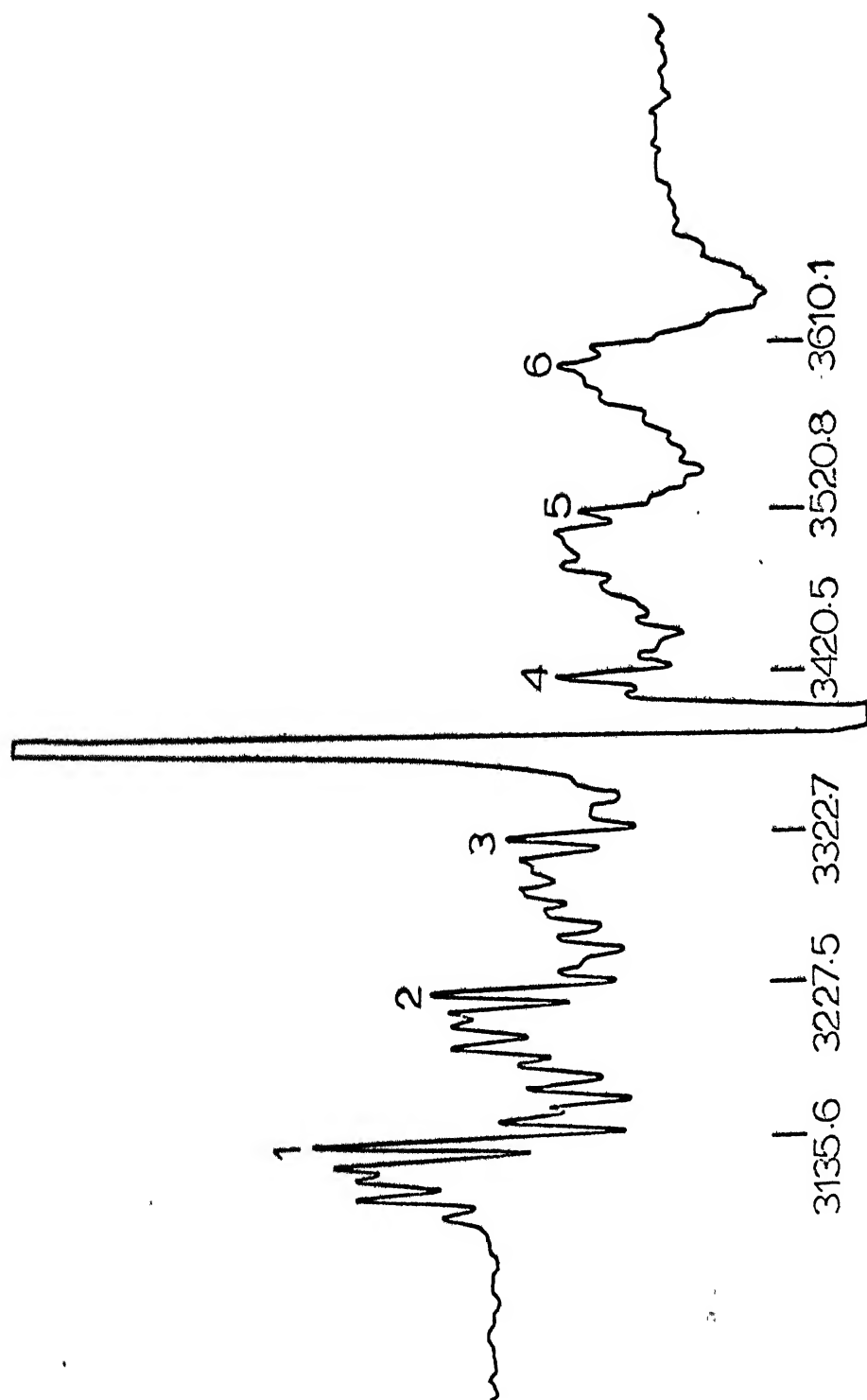


Fig. 5.1. The EPR spectrum II of  $\text{Mn}^{2+}$ : NaF powdered (Polycrystalline) sample at room temperature. Numbers indicate the field values in gauss. The central line is due to the field marker, DPPH.

It may be noted that one would be tempted to analyse the spectrum  $\text{III}_4$  as a  $90^\circ$  part of the spectrum  $\text{III}_2$ . Then one should see two components for  $\text{III}_2$  when H is deviated from the  $\langle 100 \rangle$  direction and such components have not been observed. Further, the spectrum  $\text{III}_4$  is about ten times more intense than spectrum  $\text{III}_2$  which will be difficult to understand unless these two are different spectra. A detailed analysis for these spectra confirmed that they are two different spectra. It appears that the  $\theta = 90^\circ$  spectrum of  $\text{III}_2$  is overlapped by the stronger spectrum  $\text{III}_4$  and is not identifiable separately. Similarly the  $\theta = 90^\circ$  part of the spectrum  $\text{III}_4$  is overlapped by the spectrum II and is not observable.

## 5.5 EFFECT OF TEMPERATURE

High temperature studies are made up to  $573^\circ\text{K}$ . One expects that the vacancies become mobile and get dissociated from  $\text{Mn}^{2+}$  ions at higher temperatures<sup>14,15</sup>. In the present study the intensity of the axial and cubic spectra increased in the first instance with the increase of temperature indicating that the number of the corresponding magnetic centres has increased in the initial stages. This happens probably at the expense of the intensity of the spectrum I which is found to be more prominent at the  $93^\circ\text{K}$ . On further increase of temperature, at about  $533^\circ\text{K}$  the 'SHFS' gets smeared up and the intensity of the

axial spectra start diminishing with a corresponding increase in the intensity of the cubic spectrum. One can infer from these observations that the charge compensation is occurring by the production of alkali vacancies and the vacancies become mobile above 533 °K and get dissociated at higher temperature thus making the local symmetry of  $\text{Mn}^{2+}$  cubic. This is reflected in the exchange of intensities between axial and cubic spectra, the intensity of the latter being enhanced at the cost of the intensity of the former.

The superhyperfine structure has been analysed following the procedure of Tinkham<sup>12</sup>. Here it may be mentioned that Clogston, Gordon, Jaccarino, Peter and Walker<sup>16</sup> have reported an extensive work on  $\text{F}^{19}$  superhyperfine structure in the EPR spectrum of  $\text{Mn}^{2+}$  in  $\text{ZnF}_2$  and improved the work done earlier by Tinkham<sup>12</sup>. Clogston et al<sup>16</sup> worked at 23.3 and 54 GHz and obtained  $\Delta m_F = \pm 1$  transitions apart from  $\Delta m_F = 0$  in the observed SHFS. However, the present experimental conditions and the observed SHFS are more similar to that of Tinkham's and may be classified as "simple" in the notation of Clogston et al<sup>16</sup>. A comparison of the observed and calculated SHFS pattern for the transition  $M = +5/2 \rightarrow +3/2$ ,  $m = -5/2 \rightarrow -5/2$  in the spectra  $\text{III}_2$  and  $\text{III}_4$  is shown in Tables (5.1) and (5.2) respectively while that for the transition  $M = +1/2 \rightarrow -1/2$ ,  $m = -5/2 \rightarrow -5/2$  in the spectrum II is shown in Table (5.3).



TABLE II

The observed and calculated superhyperfine structure in spectrum III<sub>4</sub> with  $A_S = 14.3G$   
 and  $A_\sigma = 3.8G$   
 ( $M = +5/2 \rightarrow +3/2$  and  $m = -5/2 \rightarrow -5/2$ )

Relative statistical weight	$\delta H$	$\delta H$ in gauss	$\delta H$ expected peaks in gauss	Calculated relative intensity	$H$ (calculated) $= \delta H + 2704.0$ in gauss	$H$ observed in gauss	Observed relative intensity
1	$-3A_S$	-42.9	-42.9	1	2661.1	2662.1	1
4	$-(2A_S + A_\sigma)$	-32.4	-32.4	4	2671.6	2672.0	3
6	$-(A_S + 2A_\sigma)$	-21.9	-21.9	8	2682.3	2682.0	8
2	$-2(A_S - A_\sigma)$	-21.0	-21.0				
4	$-3A_\sigma$	-11.4	-10.8	12	2693.2	2693.8	12
8	$-(A_S - A_\sigma)$	-10.5					
1	$(A_S - 4A_\sigma)$	-0.9					
12	0	0.0	0.0	14	2704.0	2703.1	14
1	$-(A_S - 4A_\sigma)$	0.9					
8	$(A_S - A_\sigma)$	10.5	10.8	12	2714.8	2714.8	12
4	$3A_\sigma$	11.4					
2	$2(A_S - A_\sigma)$	21.0	21.7	8	2725.7	2726.0	8
6	$(A_S + 2A_\sigma)$	21.9					
4	$(2A_S + A_\sigma)$	32.4	32.4	4	2736.4	2736.7	4
1	$3A_S$	42.9	42.9	1	2746.9	2747.2	1

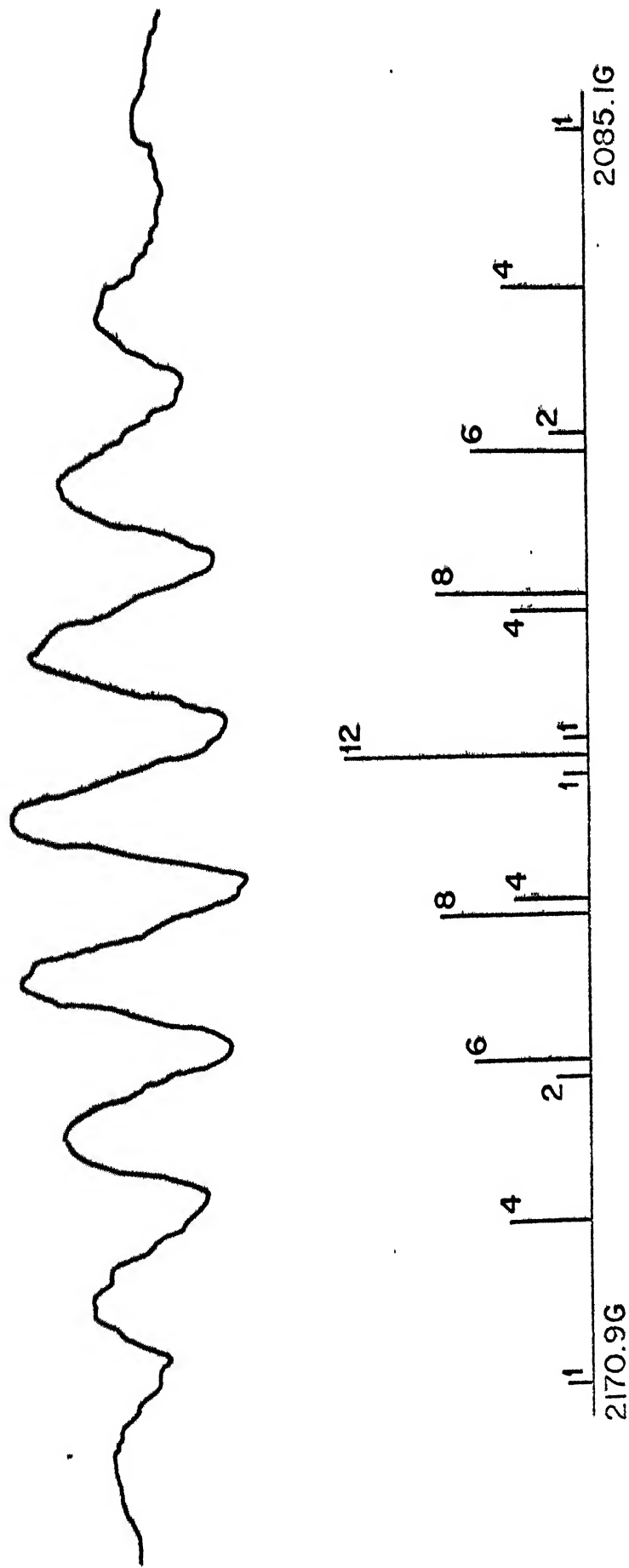


Fig. 5.2. The observed and calculated superhyperfine structure in the EPR spectrum  $\text{III}_2$  of  $\text{Mn}^{2+}$ : NaF single crystal at room temperature with H parallel to the (100) axis of the crystal for the transition  $M = +5/2 \rightarrow +3/2$  and  $m = -5/2 \rightarrow -5/2$ .

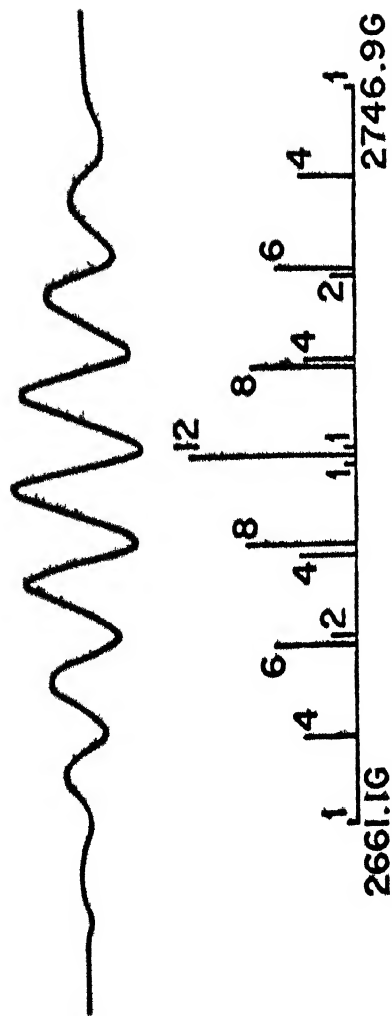


Fig. 5.3. The observed and calculated superhyperfine structure in the EPR spectrum  $\text{III}_4$  of  $\text{Mn}^{2+}$ : NaF single crystal at room temperature with H parallel to the (100) axis of the crystal for the transition  $M = +5/2 \rightarrow +3/2$  and  $m = -5/2 \rightarrow -5/2$ .

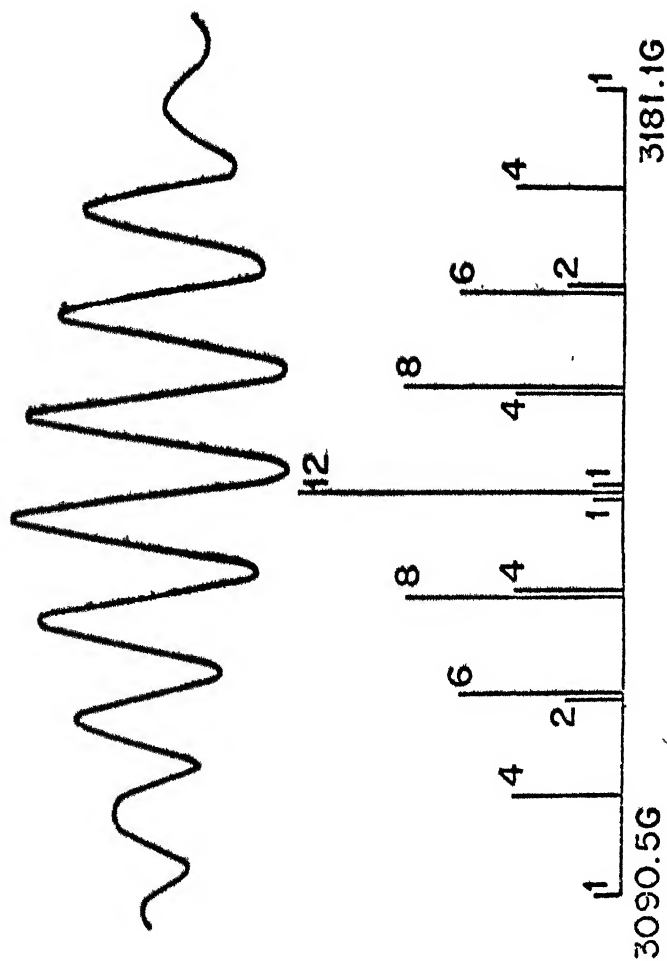


Fig. 5.4. The observed and calculated superhyperfine structure in the EPR spectrum II of  $\text{Mn}^{2+}$ : NaF single crystal at room temperature with H parallel to the (100) axis of crystal for the transition  $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$  and  $m = -\frac{5}{2} \rightarrow -\frac{5}{2}$ .

The observed and calculated superhyperfine structure in spectrum II with  $A_S = 15.13$   
 and  $A_O = 3.73$   
 ( $M = +1/2 \leftrightarrow -1/2$  and  $m = -5/2 \leftrightarrow -3/2$ )

Line Nos.	Relative statistical weight	$\delta H$	$\delta H$ in gauss	$\delta H$ expected peaks in gauss	Calculated relative intensity	H=III+ 3135.3 in gauss	H observed in gauss	Observed relative intensity
1	1	$-3A_S$	-45.3	-45.3	1	3090.5	3091.4	1
2	4	$-(2A_S + A_O)$	-33.9	-33.9	4	3101.9	3102.4	4
3	2	$-2(A_S - A_O)$	-22.8	-22.8	8	3113.2	3112.6	8
4	6	$-(A_S + 2A_O)$	-22.5	-22.5				
5	8	$-(A_S - A_O)$	-11.4	-11.3	12	3124.5	3123.7	13
6	4	$-3A_O$	-11.1					
7	1	$-(A_S - 4A_O)$	-0.3					
8	12	0	0	0	14	3135.8	3135.6	14
9	1	$(A_S - 4A_O)$	0.3					
10	4	$3A_O$	11.1	11.3	12	3147.1	3146.7	13.5
11	8	$(A_S - A_O)$	11.4					
12	6	$(A_S + 2A_O)$	22.5	22.6	8	3158.4	3157.7	10
13	2	$2(A_S - A_O)$	22.8					
14	4	$(2A_S + A_O)$	33.9	33.9	4	3169.7	3169.6	6
15	1	$3A_S$	45.3	45.3	1	3181.1	3182.4	2

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## CHAPTER VI

ELECTRON PARAMAGNETIC RESONANCE  
of  $\text{VO}^{2+}$  IN THE ALKALI CHLORIDES

## ABSTRACT

Electron paramagnetic resonance (EPR) of  $\text{VO}^{2+}$  radicals incorporated in face-centred single crystals of NaCl, KCl and RbCl has been studied in the temperature range of 77 °K to 330 °K. At liquid nitrogen temperature, anisotropic spectra have been recorded in each case while spectra recorded at room and higher temperatures are isotropic suggesting the existence of a fast readjustment of  $\text{VO}^{2+}$  molecular ions in the crystals at higher temperature while this motion gets hindered at liquid nitrogen temperatures. Spin-Hamiltonian constants are calculated from the recorded isotropic and anisotropic spectra. The line widths in each case are found to obey a parabolic law originally proposed by Kivelson. The constants which give a close fit have been evaluated. The random orientation and readjustment of V-O bond in these alkali chloride crystals is explained on the assumption that the medium exhibits a "liquid-like" nature for  $\text{VO}^{2+}$  molecular ion as far as the electron paramagnetic resonance absorption is concerned.



## 6.1 INTRODUCTION

Electron paramagnetic resonance (EPR) of  $\text{VO}^{2+}$  doped in  $\text{NH}_4\text{Cl}$  single crystal has been recently studied by Sastry and Venkateswarlu<sup>1</sup> and that in  $\text{KNO}_3$  and  $\text{CsNO}_3$  by Rao, Sastry and Venkateswarlu<sup>2</sup>. It has been found from these studies that the molecular ion  $\text{VO}^{2+}$  does not have a fixed orientation in these crystals and undergoes a fast readjustment at room temperature while it shows the effects of hindered rotation at low temperatures. On the other hand,  $\text{VO}^{2+}$  is known to have preferred orientation in Tutton salts<sup>3</sup> and in rubidium and caesium alums.<sup>4</sup> Very recently Rao, Sastry and Venkateswarlu<sup>5</sup> have also found from their EPR studies that the  $\text{VO}^{2+}$  ion has preferred orientation in the potassium and ammonium aluminium alums and MAG alum. The present work has been undertaken to get information about the  $\text{VO}^{2+}$  complex in the alkali halide crystals,  $\text{NaCl}$ ,  $\text{KCl}$  and  $\text{RbCl}$ . Further it was felt that if these systems exhibit a "liquid-like" behaviour they might represent better examples than  $\text{NH}_4\text{Cl}:\text{VO}^{2+}$ ,  $\text{KNO}_3:\text{VO}^{2+}$  and  $\text{CsNO}_3:\text{VO}^{2+}$  to examine the applicability of Kivelson's theory<sup>6</sup> of paramagnetic relaxation in liquids as these crystals (alkali halides) exhibit a liquid-like nature as far as  $\text{VO}^{2+}$  is concerned.

## 6.2 EXPERIMENTAL PROCEDURE

0.5 mol percent of vanadyl chloride is added to E. Merck, A.R. Quality chlorides of sodium, potassium and rubidium. Slow evaporation of aqueous solution yielded well-developed cubes. EPR measurements are carried at

X-band, 9.5 kMc/sec. nominal frequency, with a Varian V-4502 EPR spectrometer and a V-3400 nine-inch rotating electromagnet using a 100 kc/sec field modulation. The magnetic field is calibrated using DPPH\* as a field marker. The proton resonance is monitored with a Varian Flux-meter model F-8A connected to a Beckmann 10-110 Mc/sec. convertor 7571. Spectra are recorded at various temperatures ranging from +60 °C to -180 °C with the help of a Varian V-4540 variable temperature accessory. General microwave 459A thermoelectric power meter has been used for measuring the power output. IBM electronic computers 1620 and 7044 have been used for calculations and least square fit.

### 6.3 THEORY

The electronic state of the  $\text{VO}^{2+}$  ion is mainly dependent on the  $3d^1$  electron of vanadium. In a crystalline field of symmetry less than cubic the lowest level will be an orbital singlet. In such a case only one fine structure transition can be expected in EPR, and the hyperfine structure would show eight lines because of the  $\text{V}^{51}$  nucleus whose spin is  $7/2$ . As the EPR is due to the molecular ion which has itself an axial field, the spectrum cannot be expected to reveal cubic site symmetry even if  $\text{VO}^{2+}$  goes in substitutionally and the expected positive vacancy is too far off from it. If the  $\text{VO}^{2+}$  ion goes in substitutionally in the present alkali halides as  $\text{Mn}^{2+}$

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\*Diphenylpicrylhydrazyl whose g-value is taken as 2.0036

in NaCl, it might get associated with a first neighbour positive vacancy in which case the site symmetry will be orthorhombic or it might get associated with a second neighbour positive vacancy in which case the site symmetry will be tetragonal. However, the EPR spectra of  $\text{VO}^{2+}$  obtained in the present experiments are found to be independent of the crystal orientation with respect to the magnetic field indicating clearly that the  $\text{VO}^{2+}$  ion has no preferred orientation in the present crystals.

For a paramagnetic ion placed in a matrix which does not exhibit directional properties the spectra can be interpreted using a simple model of random array<sup>7</sup> of magnetic ions. The EPR spectrum of  $\text{VO}^{2+}$  in tetragonal symmetry or of randomly oriented  $\text{VO}^{2+}$  molecular ions in solutions can be described by the spin-Hamiltonian,<sup>8-10</sup> of the type

$$\mathcal{H} = g_{\parallel} \beta H_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A I_z S_z + B(I_x S_x + I_y S_y). \quad \dots \quad (6.1)$$

The Hamiltonian (6.1) leads to the following magnetic field resonance<sup>10</sup> values for the hyperfine structure components in the EPR spectrum of  $\text{VO}^{2+}$ :

$$H = H_0 - \frac{K m_I}{g_{\beta}} - \frac{B^2(A^2 + K^2)}{4 H_0 g_{\beta}^2 K^2} [I(I+1) - m_I^2] - \frac{(A^2 - B^2) g_{\parallel}^2 g_{\perp}^2}{2 H_0 g_{\beta}^2 K^2 g^4} \sin^2 \theta \cos^2 \theta m_I^2 \quad \dots \quad (6.2)$$

TABLE 5.4  
SPIN-HAMILTONIAN PARAMETERS\* OF  
Mn<sup>2+</sup> IN NaF AT 300 °K

Parameter	Spectrum I	Spectrum II	Spectrum III <sub>2</sub>	Spectrum III <sub>4</sub>
$g$	2.0	2.003±0.002	2.014±0.004 (2.00±0.01) <sup>†</sup>	1.995±0.003 (1.996±0.006) <sup>†</sup>
$A_{55}^{55}$ x10 <sup>-4</sup> cm <sup>-1</sup>	..	-90.4±1.6 (88.6±0.1) <sup>§</sup>	-92.8±0.5 (92±4) <sup>†</sup>	-93.8±1.0 (91±4) <sup>†</sup>
$D$ x10 <sup>-4</sup> cm <sup>-1</sup>	..	...	221.0±0.2 (225±8) <sup>†</sup>	89.0±0.5 (89±5) <sup>†</sup>
$a$ x10 <sup>-4</sup> cm <sup>-1</sup>	..	...	0.2	-1.3
$A_{19}^{19}$ x10 <sup>-4</sup> cm <sup>-1</sup>	..	14.2±0.4 (12.9±0.2) <sup>§</sup>	13.4±0.2	13.3±0.3 (14.4±0.3) <sup>†</sup>
$A_{\sigma}^{19}$ x10 <sup>-4</sup> cm <sup>-1</sup>	..	3.5±0.6 (3.2±0.2) <sup>§</sup>	3.1±0.3	3.5±0.5 (2.8±0.7) <sup>†</sup>

\* It is to be noted that the constants  $A_s$  and  $A_{\sigma}$  are given in units of 10<sup>-4</sup>cm.<sup>-1</sup> here while they are given in gauss in Tables (5.1), (5.2) and (5.3).

<sup>†</sup> These values are those obtained by Hayes and Jones<sup>3</sup> at 90 °K.

<sup>§</sup> Hall, Hayes, Stevenson and Wilkens<sup>13</sup>.

is also angular independent. Figs. 6.1 and 6.2 show the typical spectra obtained in the case of  $\text{NaCl:VO}^{2+}$  system. The parallel and perpendicular components are labelled "a" and "b" respectively. The gradual change of spectrum to spectrum II with lowering of temperature is reversible. The isotropic spectrum I is similar to those reported by Rao et al<sup>2</sup> in the case of  $\text{CsNO}_3\text{:VO}^{2+}$  and  $\text{KNO}_3\text{:VO}^{2+}$  at room temperature, and O'Reilly<sup>8</sup> for Vanadyl etioporphirin I (VEPI) in benzene solution. On the other hand, the anisotropic spectrum II obtained at liquid nitrogen temperature as in the case of  $\text{KNO}_3$ ,  $\text{CsNO}_3$  and  $\text{NH}_4\text{Cl}$ <sup>1,2</sup> is similar to the spectrum obtained by Hochstrasier<sup>11</sup> for  $\text{VO}^{2+}$  in amorphous glass and to those obtained by O'Reilly<sup>8</sup> for VEPI dissolved in high viscous petroleum oil and for solid asphaltenes containing vanadium. This similarity suggests that the  $\text{VO}^{2+}$  in alkali chlorides behaves as if it were in a liquid medium as far as the results of EPR are concerned. The isotropic spectrum at room temperature is probably due to a fast reorientation of the V-O bond which results in the averaging out of anisotropies in g and A tensors. As the temperature is lowered, the fast reorientation gets hindered and at liquid nitrogen temperature the reorientation rate is slow enough that the anisotropies in g and A tensors are not averaged out and can be seen in the spectrum. However, even at liquid nitrogen temperature the orientation of the V-O bond is random enough to make the EPR spectrum angular independent. The appearance of

spectrum II only at liquid nitrogen temperature is probably due to the hindrance (or freezing) of the motion of  $\text{VO}^{2+}$  ion due to the lowering of temperature and as such appears to be a purely temperature effect as unlike in  $\text{NH}_4\text{Cl}$  there are no phase transformations in the crystals studied here.

O'Reilly<sup>8</sup> and McConnell<sup>13</sup> obtained the following expressions for the isotropic values of  $g$  and  $A$  in terms of  $g_{\parallel}$  and  $g_{\perp}$  for the cases where the molecule is rotating with a correlation time much shorter than the reciprocal of the frequency spread of this spectrum:

$$g_0 = \frac{g_{\parallel} + 2g_{\perp}}{3} \quad \dots (6.3a)$$

$$A_0 = \frac{A + 2B}{3} \quad \dots (6.3b)$$

The values obtained for  $g_0$  and  $A_0$  from the analysis of the spectrum I are listed in Table 6.1 for the different alkali halides studied.

The Hamiltonian (6.1) remains anisotropic for cases where the correlation time is long. The existence of anisotropic spectra at liquid nitrogen temperature in all cases is confirmed by varying the microwave power level from 1.0 mW to 110  $\mu$ W. There were no saturation effects and the intensities followed the power levels, their relative values remaining the same.

TABLE 6.1

Spin-Hamiltonian Constants for  $\text{VO}^{2+}$  in  
NaCl and RbCl Single Crystals

(Values of  $A_0$ ,  $A_{||}$  and  $A_{\perp}$  are in units of  $10^{-4}\text{cm}^{-1}$ )

Crystal System	Spectrum I	Spectrum II
$\text{NaCl:VO}^{2+}$	$g_0 = 1.971 \pm 0.001$	$g_{  } = 1.925 \pm 0.002$
	$A_0 = 104.0 \pm 1.0$	$g_{\perp} = 1.996 \pm 0.002$
$\text{KCl:VO}^{2+}$		$A_{  } = 176.8 \pm 2.0$
		$A_{\perp} = 64.2 \pm 2.0$
	$g_0 = 1.969 \pm 0.002$	$g_{  } = 1.932 \pm 0.002$
	$A_0 = 106.8 \pm 2.0$	$g_{\perp} = 1.988 \pm 0.002$
		$A_{  } = 186.8 \pm 3.0$
$\text{RbCl:VO}^{2+}$		$A_{\perp} = 70.4 \pm 5.0$
	$g_0 = 1.967 \pm 0.002$	$g_{  } = 1.939 \pm 0.002$
	$A_0 = 106.0 \pm 2.0$	$g_{\perp} = 1.968 \pm 0.002$
		$A_{  } = 188.7 \pm 3.0$
		$A_{\perp} = 63.9 \pm 3.0$

All the spectra obtained, type I and type II, have been analyzed using equation (6.2) and the results are tabulated in Table (6.1).

## 6.5 LINE WIDTH STUDIES

The spin resonance studies have clearly shown that  $\text{VO}^{2+}$  in alkali chlorides exhibit a "liquid-like" nature as far as the paramagnetic resonance and relaxation are concerned similar to what has been reported earlier in the case of  $\text{NH}_4\text{Cl}$ <sup>1</sup>,  $\text{KNO}_3$  and  $\text{CsNO}_3$ <sup>2</sup>. An attempt is therefore made to see the applicability of Kivelson's theory<sup>6</sup> of paramagnetic relaxation in liquids, to the single crystal systems of the present study.

It has been shown<sup>6,13</sup> that the anisotropies in  $g$  and  $A$  tensors contribute to the line broadening in the EPR spectra. When there are considerable anisotropies in  $g$  and  $A$ , the line widths can be given by the following expression<sup>14</sup>

$$1/t_2 = a_1 + a_2 m_I + a_3 m_I^2 \quad \dots (6.4)$$

where  $a$ 's<sup>+</sup> depend upon the factors  $(g_{\parallel} - g_{\perp})$  and  $(A - B)$ . The experimental line widths are measured by the method used by Rogers and Pake<sup>14</sup> and Rao et al<sup>2</sup> where it is

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<sup>+</sup>The  $a$ 's given here are related to those in reference 14 by a multiplicative constant  $\pi\sqrt{3}$ .



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where  $a$ 's<sup>+</sup> depend upon the factors  $(g_{||} - g_{\perp})$  and  $(A - B)$ . The experimental line widths are measured by the method used by Rogers and Pake<sup>14</sup> and Rao et al<sup>2</sup> where it is

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\*The  $a$ 's given here are related to those in reference 14 by a multiplicative constant  $\pi\sqrt{3}$ .

assumed that the population difference between the different  $m_I$  levels is small. The  $m_I$  dependence of the line widths is shown in Figs. 6.3, 6.4 and 6.5. These curves fit in very well with equation (6.4), and a least square calculation yields the constants  $a_1$ ,  $a_2$  and  $a_3$  given in Table 6.2. Wilson and Kivelson<sup>15</sup> have added cubic and fourth order terms to the polynomial in equation 6.4; but such terms are not found to be necessary in the present case.

TABLE 6.2

Line Width Parameters of the EPR of  $\text{VO}^{2+}$   
in Alkali Halides

Crystal	$a_1$ in gauss	$a_2$ in gauss	$a_3$ in gauss
NaCl	23.40	2.30	1.23
KCl	19.40	1.30	0.54
RbCl	20.13	1.62	0.72

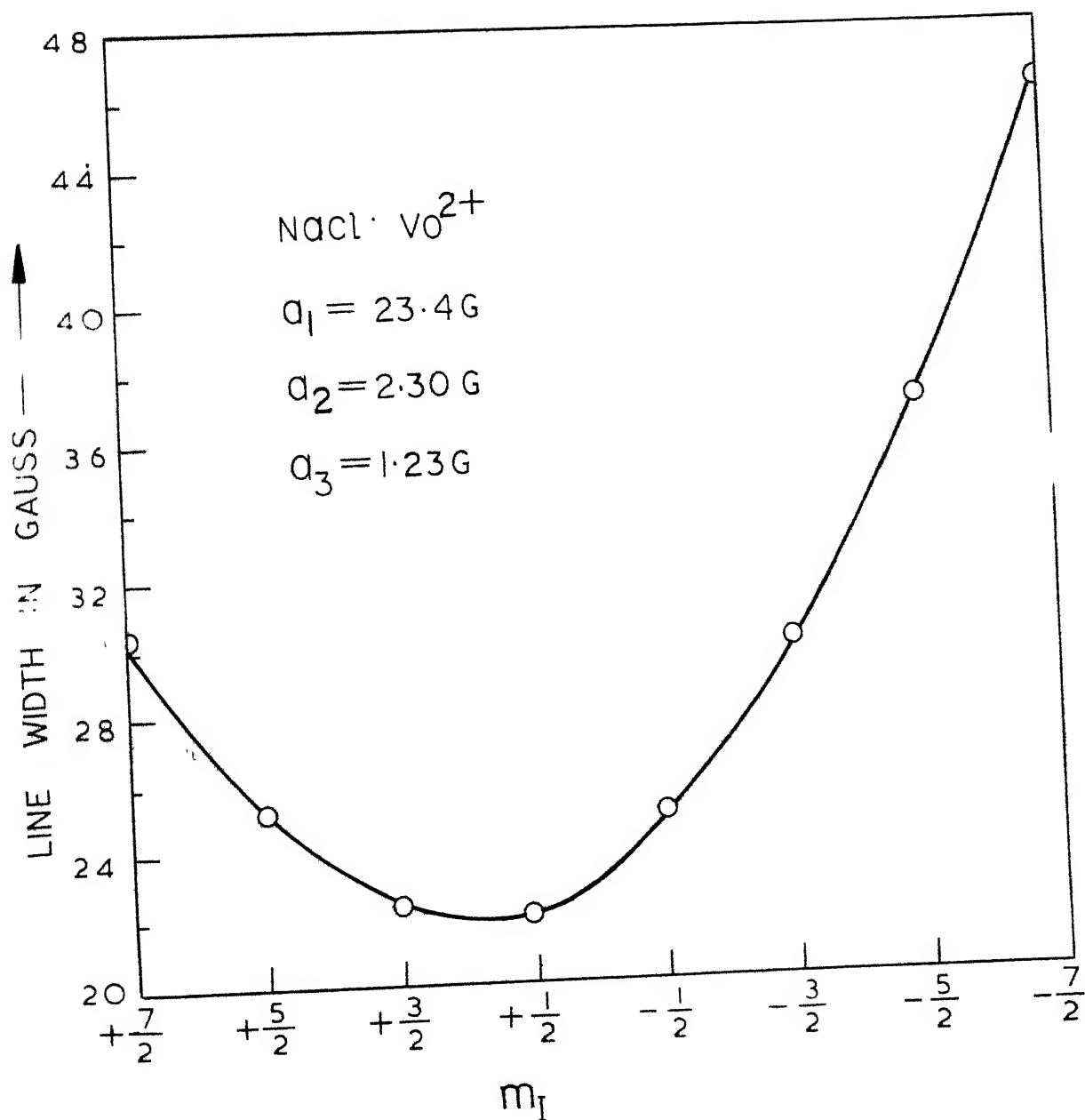


FIG. 6-3 PLOT OF LINE WIDTH VERSUS  $m_I$  IN THE EPR OF  $\text{NaCl}:\text{VO}^{2+}$  SYSTEM. THE SOLID CURVE REPRESENTS PREDICTED VARIATION OF THE LINE WIDTH WHILE CIRCLES INDICATE ACTUAL EXPERIMENTAL VALUES AT ROOM TEMPERATURE

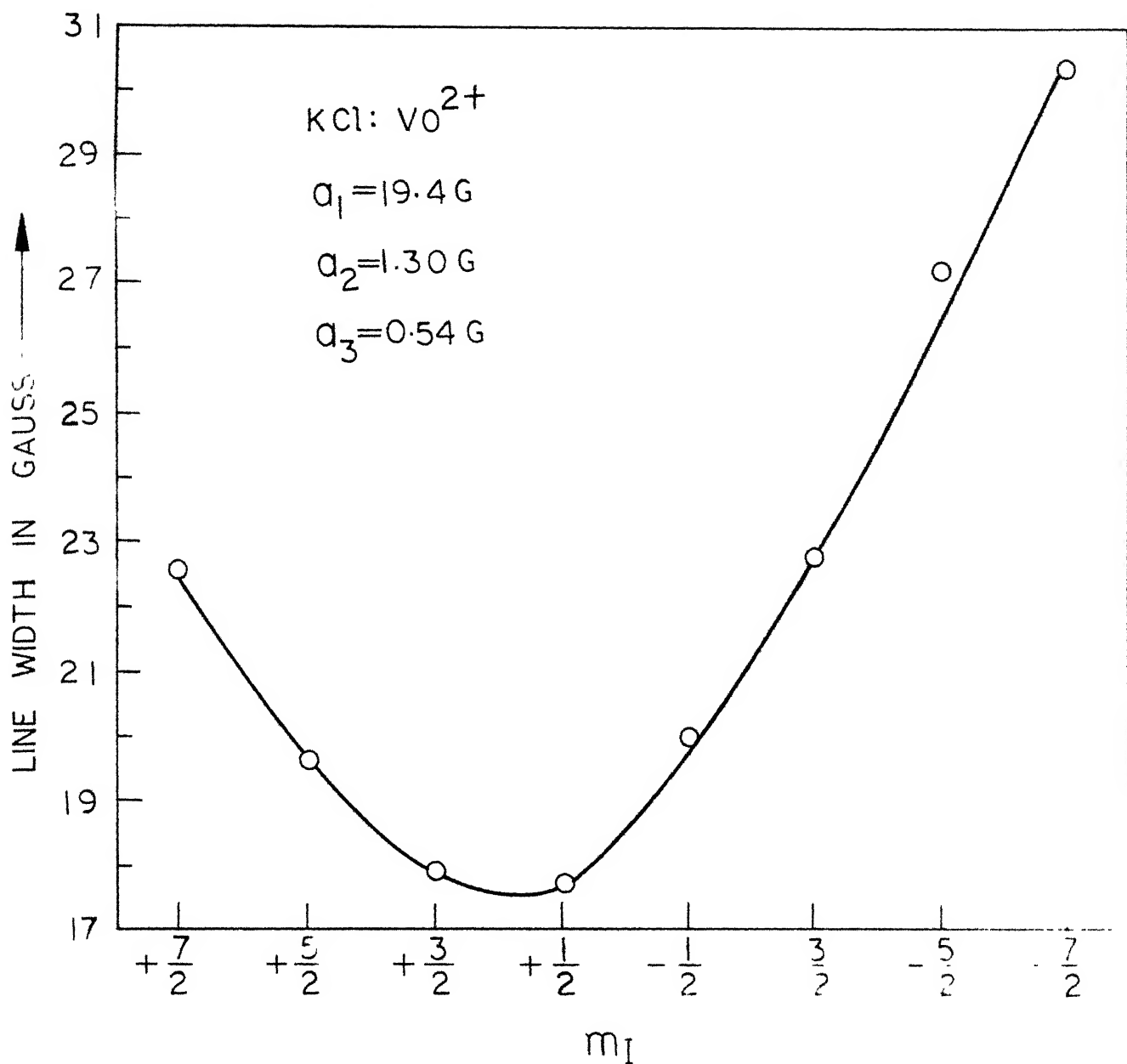


FIG. 6-4 PLOT OF LINE WIDTH VERSUS  $m_I$  IN THE EPR OF  $\text{KCl:VO}^{2+}$  SYSTEM.  
 THE SOLID CURVE REPRESENTS PREDICTED VARIATION OF THE LINE  
 WIDTH WHILE CIRCLES INDICATE ACTUAL EXPERIMENTAL VALUES  
 AT ROOM TEMPERATURE.

## APPENDICES A and B

Appendix A comprises of two Tables, 7.1 and 7.2 which list respectively the spin Hamiltonian constants of the divalent ions  $\text{Mn}^{2+}$  and  $\text{VO}^{2+}$  studied in this thesis when they are doped in different host lattices. Appendix B contains some of the computer programs used in calculations.

TABLE 7.1

 $Mn^{2+}$ 

Crystal	g	D	E	A	Reference	Note
Diopside	2.0017	452.95	-102.8	84.4	7.1	a
$CaMgSi_2O_6$	2.0016	G	G	G		
	2.0016			84.4		
	2.0015	379.84	17.09	81.9	7.1	a
	2.0013	G	G	91.3		
	2.0008			91.7		
				90.8		
Tremolite	1.998	-448.3	-78.2	77.9	7.2	b
$2(H_2Ca_2Mg_5(SiO_3)_8)$	1.997	G	G	G		
	1.995	-442.9	-79.4	76.7	7.2	b
	1.993	G	G	79.9		
				79.0		
Spodumene	2.0013	579	81.3	89.5	7.3	c
(Kunzite)	2.0011	G	G	G		
LiAl- ( $SiO_3$ ) <sub>2</sub>	2.0012	947	122	87.5	7.3	c
	2.0024	G	G	88.3		
				83.9		
$Cd_2V_2O_7$	2.0004	-418	+41.7	-86.7	7.4	d
	1.9995	G	G	G		
	2.0001			-87.0		
				-87.4		
$NH_4Cl$	2.0012	1603.6		88.6	7.5	e
	2.0012	G		G		
				90.7		
NaCl	1.95	-1450	107	-85	7.6	f
		G	G			
$MnBCl_2 \cdot 6H_2O$	2.01	1300			7.7	g
		G				

TABLE 7.1 (CONTINUED)

 $Mn^{2+}$ 

Crystal	g	D	E	A	Reference	Note
$Cs_2SO_4$	2.000	941 Oe	14 Oe	93 Oe	Present work	p
	2.015			91 "		
	2.000			91 "		



TABLE 7.2  
VO<sup>2+</sup> or V<sup>4+</sup>

Crystal	$g$	$A$	Reference	Note
TiO <sub>2</sub>	$g_x=1.915$	$A_x=0.0031 \text{ cm}^{-1}$	7.8	h
	$g_y=1.913$	$A_y=0.0043 \text{ cm}^{-1}$		
	$g_z=1.956$	$A_z=0.0142 \text{ cm}^{-1}$		
Sapphire	$g_{  }=1.97$	$A_{  }=0.0132 \text{ cm}^{-1}$	7.9	i
GeO <sub>2</sub>	$g_{  }=1.929$	$A_{  }=175.5 \times 10^{-4} \text{ cm}^{-1}$	7.10	j
	$g_{\perp}=1.976$	$A_{\perp}=68.2 \times 10^{-4} \text{ cm}^{-1}$		
GeO <sub>2</sub>	$g_z=1.963$	$A_z=134.36 \times 10^{-4} \text{ cm}^{-1}$	7.10	k
	$g_x=1.921$	$A_x=36.69 \text{ "}$		
	$g_y=1.921$	$A_y=37.54 \text{ "}$		
Zn(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	$g_x=1.9813$	$A_x=0.007120 \text{ cm}^{-1}$	7.11	l
	$g_y=1.9801$	$A_y=0.007244 \text{ "}$		
Tutton salt	$g_z=1.9331$	$A_z=0.018281 \text{ "}$		
K <sub>2</sub> V <sub>2</sub> O <sub>7</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> · 4H <sub>2</sub> O	$g_1=1.95_4$		7.12	m
	$g_2=1.98_5$			
	$g_3=1.96_7$			
Rb Alum	$g_{  }=1.932$	$A=182.2 \times 10^{-4} \text{ cm}^{-1}$	7.13	
	$g_{\perp}=1.975$	$B=66.6 \text{ "}$		
Cs Alum	$g_{  }=1.932$	$A=183.4 \text{ "}$		
	$g_{\perp}=1.979$	$B=65.7 \text{ "}$		
Potassium Alum	$g_{  }=1.936$	$A=177 \text{ "}$	7.14	n
	$g_{\perp}=1.977$	$B=68 \text{ "}$		
Ammonium Alum	$g_{  }=1.940$	$A=176.0 \text{ "}$	7.14	n
	$g_{\perp}=1.978$	$B=67 \text{ "}$		
Triglycine Sulphate	$g_{  }=1.922$	$A=179.3 \text{ "}$	7.15	o
	$g_{\perp}=1.974$	$B=70.4 \text{ "}$		

TABLE 7.2(CONTINUED)

Crystal	$g$	$A$	Reference	Note
Caesium sulphate	$g_z=1.9382$	$A_z=197.0$ oe	Present work	q
	$g_x=1.9963$	$A_x=77.5$ "		
	$g_y=1.9947$	$A_y=81.5$ "		
	$g_z=1.9669$	$A_z=143.0$ "	"	"
	$g_x=1.9992$	$A_x=65.5$ "		
	$g_y=1.9963$	$A_y=77.5$ "	"	"
	$g_z=1.9498$	$A_z=179.0$ "		
	$g_x=2.0006$	$A_x=76.0$ "		
	$g_y=1.9939$	$A_y=82.0$ "		

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Notes to Tables 7.1 and 7.2

- (a) Work was done at two approximate frequencies of 10 Gc/s and 36 Gc/s.  
Two complexes have been observed.  
The error in  $g_z$  is 0.0005 while the error in  $g_x$  and  $g_y$  is 0.0008.  
The error in hyperfine constant is 0.5G  
For complex I  $b_4^0=0.34$ ,  $b_4^2=-4.74$ ,  $b_4^4=15.88$  G.  
For complex II  $b_4^0=-6.58$ ,  $b_4^2=-2.93$ ,  $b_4^4=32.47$  G.  
Error in D and E is not stated.
- (b) Work was done at 9.2 GHz.  
Values are given for two varieties, pink tremolite and white tremolite.  
The error in  $g_z$  and  $g_y$  is 0.001  
The error in hyperfine constant is 0.5G

For pink tremolite  $b_4^0 = -0.96$ ,  $b_4^2 = 33.0$ ,  $b_4^4 = -34.6$  G  
 For white tremolite  $b_4^0 = -0.43$ ,  $b_4^2 = -19.0$ ,  $b_4^4 = 18.2$  G

- (c) Work was done at k-band frequencies  
 As many as 6 complexes are reported  
 The error in g's is 0.0003 for complex I  
 The error in g's is 0.0005 for complex VI  
 The error in D is 2G for complex I and 15G for complex VI.  
 The error in E is 1G for complex I and 5G for complex VI.  
 The error in  $A_z$ ,  $A_y$  is 0.5G for complex I  
 The error in  $A_z$  is 4G and that in  $A_y$  is 2G for complex VI.  
 For complex I  $b_4^0 = -1 \pm 2$  G,  $b_4^2 = -4 \pm 2$  and  $b_4^4 < 0.5 \pm 2$  G.  
 The direction cosines of the ESR spectral axes with relative signs are:

Spectrum	Complex I	Complex VI	Axis
x	0	0.26989	<u>bxc</u>
	-1	-0.55335	<u>b</u>
	0	0.78801	<u>c</u>
y	0.91355	0.80115	<u>bxc</u>
	0	-0.58207	<u>b</u>
	-0.40674	-0.13917	<u>c</u>
z	+0.40674	0.57449	<u>bxc</u>
	0	0.55478	<u>b</u>
	0.91355	0.60182	<u>c</u>

- (d) Work was done at 35 Gc/s  
 Error in g-values is 0.0008  
 Error in D is 1G while that in E is 2G  
 Error in  $A_x$  is 3G,  $A_y$  is 10G and  $A_z$  is 5G  
 $b_4^0 = -1 \pm 1$ ,  $b_4^2 = 1 \pm 6$ ,  $b_4^4 = -15 \pm 7$
- (e) Work was done at 37 Gc/sec and 51 Gc/sec  
 0.01% manganese as  $MnCl_2$  added to  $NH_4Cl$  with pectin to get doped single crystals.  
 Error in A and B is 0.5G  
 Error in g's is 0.0005.  
 Cubic field constant referred to as  $D_4$  is  $-2.3 \pm 0.5$  G.

- (f) Work was done at k-band spectrum  
Doped crystals were x-irradiated  
Error in  $g$  is 0.01; error in  $A$  is 1G and error  
in  $E$  is 10G.  
Cubic field parameter  $a$  is 40G.
- (g) A typical five line spectrum is obtained  
Manganese is in spin 5/2 state  
 $B$  is a macroscopic ligand  
 $b_4^0=0$ ,  $b_4^4 = -100G$   
Absolute signs are not determined but the sign of  
 $b_0^2$  is opposite to that of  $b_4^4$ .
- (h) Rutile form of  $TiO_2$ ; nearly tetragonal  $z$ -axis.  
Direction cosines of the magnetic axes relative  
to the crystal axes are:

	$a$	$a$	$c$
$x$	$-\sqrt{E}/2$	$\pm\sqrt{E}/2$	0
$y$	0	0	1
$z$	$\pm\sqrt{E}/2$	$\sqrt{E}/2$	0

- (i) Axial crystal;  $g$  is isotropic
- (j) Amorphous; this is attributed to  $VO^{2+}$   
Error in  $g$ 's is 0.001; error in  $A$ 's is  $0.1 \times 10^{-4} \text{cm}^{-1}$ .
- (k) Tetragonal; vanadium appears as  $V^{4+}$   
Error in  $g_z$  is 0.0003; error in  $g_x$  is 0.0006 and  
error in  $g_y$  is 0.0001  
Error in  $A_z$  is  $0.02 \times 10^{-4} \text{cm}^{-1}$   
Error in  $A_x$  and  $A_y$  is  $0.01 \times 10^{-4} \text{cm}^{-1}$ .
- ( ) Work was done at x-band  
 $g$  and  $A$  tensors displaced by  $23^\circ 20'$   
 $V-O$  axis is found to have three possible orientations.
- (m) Work was done at two temperatures  $290^\circ K$  and  $90^\circ K$   
K.D.Bowers and J.Owen, Repts.Prog.in Phys. 18, 304(1955)
- (n) Error in  $g$ 's is 0.001; error in  $A$  and  $B$  is  $1.0 \times 10^{-4} \text{cm}^{-1}$
- (o) Ferroelectric crystal  
Error in  $g_{||}$  is 0.002 and error in  $g_{\perp}$  is 0.006  
Error in  $A$  is 2.5 and error in  $B$  is  $2.0 \times 10^{-4} \text{cm}^{-1}$ .

```
12      DO 12 I=1,5  
        SUM=SUM+DIF(I)  
        AVE=SUM/5.  
        VE=SQRTF(AVE)  
        G=PH*PPH/FNOT  
        PRINT 444, FNOT, G RD, RE, BFZ, BFT  
        PRINT 444, VE, (HC(I), I=1,5)  
444     FORMAT(6F10.4)  
555     CONTINUE  
        STOP  
        END
```

## APPENDIX B2

Computer programme used to diagonalize the 36x36 energy matrix.

Y(I) are the thirty field values of the entire spectrum  
G is the DPPH field value and BFF is  $b_4$ .

The matrix elements (Table 7.3) are generated.  
This program also can be used to either iterate or diagonalize any number of times NUM for different values of any parameter.

```

£JOB   PHR006,  TIME005  ,    PAGES025,    NAME A V J
£IBJOB
£IBFTC MAIN      NODECK
      DIMENSION X(36,36),E(36,36),H(36),HH(36),Y(30),DEF(30)
      ,HF(36)
      DIMENSION HFC(12),DEFS(30),DIS(30)
      DOUBLE PRECISION X,E,H,Y,DEF,HF,HFC,DEFS
      HDPPH=2.0036
      READ 3333,NUM
3333  FORMAT(I3)
      READ 10,(Y(I),I=1,30)
      PRINT 10,(Y(I),I=1,30)
10    FORMAT(10F8.2)
      READ 1009,G,RD,RE,AZ,AX,AY,HNOT
1009  FORMAT(1X,7F8.2)
      PRINT 1000,G,RD,RE,AZ,AX,AY,HNOT
      READ 1109,BFZ,BFT,BFF
      PRINT 1109,BFZ,BFT,BFF
1109  FORMAT(1X,3F6.1)
      NDIM=36
1011  FORMAT(6E12.5)
600   AXYS=AX+AY
      RF=SQRT(40.)
      RFF=SQRT(45.)
      RS=SQRT(72.)
      DO 555 INDEX=1,NUM
C     COMPUTE X MATRIX
      DO 5I=1,NDIM
      DO 5 J=1,NDIM
5     X(I,J)=0.
C     DIAGONAL ELEMENTS
      P=2.5*G+10.*RD/3.
      X(1,1)=P+6.25*AZ
      X(2,2)=P+3.75*AZ
      X(3,3)=P+1.25*AZ
      X(4,4)=P-1.25*AZ
      X(5,5)=P-3.75*AZ
      X(6,6)=P-6.25*AZ
      PP=1.5*G-2.*RD/3.
      X(7,7)=PP+3.75*AZ
      X(8,8)=PP+2.25*AZ
      X(9,9)=PP+0.75*AZ
      X(10,10)=PP-0.75*AZ

```

```

X(11,11) = PP-2.25*AZ
X(12,12) = PP-3.75*AZ
PPP=G/2.-8.*RD/3.
X(13,13) = PPP+1.25*AZ
X(14,14) = PPP+0.75*AZ
X(15,15) = PPP+0.25*AZ
X(16,16) = PPP-0.25*AZ
X(17,17) = PPP-0.75*AZ
X(18,18) = PPP-1.25*AZ
Q=-G/2.-8.*RD/3.
X(19,19)=Q-1.25*AZ
X(20,20)=Q-0.75*AZ
X(21,21)=Q-0.25*AZ
X(22,22)=Q+0.25*AZ
X(23,23)=Q+0.75*AZ
X(24,24)=Q+1.25*AZ
QQ=-1.5*G-2.*RD/3.
X(25,25)=QQ-3.75*AZ
X(26,26)=QQ-2.25*AZ
X(27,27)=QQ-0.75*AZ
X(28,28)=QQ+0.75*AZ
X(29,29)=QQ+2.25*AZ
X(30,30)=QQ+3.75*AZ
QQQ=-2.5*G+10.*RD/3.
X(31,31)=QQQ-6.25*AZ
X(32,32)=QQQ-3.75*AZ
X(33,33)=QQQ-1.25*AZ
X(34,34)=QQQ+1.25*AZ
X(35,35)=QQQ+3.75*AZ
X(36,36)=QQQ+6.25*AZ
DO 67 I=1,36
67   HF(I)=X(I,I)
C     OFF DIAGONAL ELEMENTS IN E
463  STEN=SQRT(10.0)*RE
      STH=SQRT(2.0)*3.0*RE
      DO 61 I=1,6
        J=I+12
61    X(I,J)=STEN
      DO 62 I=7,12
        J=I+12
      "  X(I,J)=STEN
      -  AXYD=AX-AY
        AXYS=AX+AY
C     OFF DIAGONAL ELEMENTS IN AX,AY
      X(7,2)=1.25*AXYS
      X(8,3)=1.25*RF*AXYS
      X(9,4)=1.25*RFF*AXYS
      X(10,5)=X(8,3)
      X(11,6)=X(7,2)
      X(8,1)=1.25*AXYD
      X(9,2)=1.25*RF*AXYD
      X(10,3)=1.25*RFF*AXYD

```



```

X(11,4)=X(9,2)
X(12,5)=X(8,1)
X(13,8)=1.25*RF*AXYS
X(14,9)=2.*AXYS
X(15,10)=1.25*RS*AXYS
X(16,11)=X(14,9)
X(17,12)=X(13,8)
X(14,7)=1.25*RF*AXYD
X(15,8)=2.*AXYD
X(16,9)=1.25*RS*AXYD
X(17,10)=X(15,8)
X(18,11)=X(14,7)
X(19,14)=1.25*RFF*AXYS
X(20,15)=1.25*RS*AXYS
X(21,16)=2.25*AXYS
X(22,17)=X(20,15)
X(23,18)=X(19,14)
X(20,13)=1.25*RFF*AXYD
X(22,15)=2.25*AXYD
X(21,14)=1.25*RS*AXYD
X(23,16)=X(21,14)
X(24,17)=X(20,13)
X(25,20)=1.25*RF*AXYS
X(26,21)=2.*AXYS
X(27,22)=1.25*RS*AXYS
X(28,23)=X(26,21)
X(29,24)=X(25,20)
X(26,19)=1.25*RF*AXYD
X(27,20)=2.*AXYD
X(28,21)=1.25*RS*AXYD
X(29,22)=X(27,20)
X(30,23)=X(26,19)
X(31,26)=1.25*AXYS
X(32,27)=1.25*RF*AXYS
X(33,28)=1.25*RFF*AXYS
X(34,29)=X(32,27)
X(35,30)=X(31,26)
X(32,25)=1.25*AXYD
X(33,26)=1.25*RE*AXYD
X(34,27)=1.25*RFF*AXYD
X(35,28)=X(33,26)
X(36,29)=X(32,25)

```

```

C      ADDITIONAL TERMS CONTAINING B4ZERO(BFZ),B4TWO(BFT)
      AND B4FOUR(BFF)
C      DIAGONAL TERMS
      DO 401 I=1,6
401    X(I,I)=X(I,I)+BFZ
      DO 402 I=7,12
402    X(I,I)=X(I,I)-3.0*BFZ
      DO 403 I=13,24
403    X(I,I)=X(I,I)+2.0*BFZ

```

```

DO 404 I=25,30
404 X(I,I)=X(I,I)-3.0*BFZ
DO 405 I=31,36
405 X(I,I)=X(I,I)+BFZ
C NONDIAGONAL TERMS IN E
DO 406 I=1,6
J=I+12
406 X(I,J)=X(I,J)+0.05*SQRT(10.0)*BFT
DO 407 I=7,18
J=I+12
407 X(I,J)=X(I,J)+0.25*SQRT(2.0)*BFT
DO 4071 I=19,24
J=I+12
4071 X(I,J)=X(I,J)+0.05*SQRT(10.0)*BFT
C ADDITIONAL NONDIAGONAL TERMS
DO 408 I=25,36
J=I-24
408 X(I,J)=0.25*SQRT(5.0)*BFF
DO 3 I=1,NDIM
DO 3 J=1,NDIM
3 X(J,I)=X(I,J)
PRINT 167
167 FORMAT(5X,*P,PP,PPP,Q,QQ,QQQ
PRINT 1008,P,PP,PPP,Q,QQ,QQQ
PRINT 168
168 FORMAT(5X,*DIAGONAL MATRIX ELEMENTS*)
PRINT 1008,(X(I,I),I=1,36)
C MATRIX DIAGONALIZATION ROUTINE-5116 SPACES
C ARRAYS USED X(I,J),E(I,J)(EIGENVECTORS),DIMENSION-
NDIM
250 DO 253 I=1,NDIM
DO 253 J=1,NDIM
IF(I-J)251,252,251
251 E(I,J)=0.
GO TO 253
252 E(I,J)=1.0
253 CONTINUE
200 LA=1
LB=2
BX=DABS(X(2,1))
DO 202 J=3,NDIM
JA=J-1
DO 202 I=1,JA
D=BX-DABS(X(I,J))
IF(D)201,202,202
201 BX=DABS(X(I,J))
LA=I
LB=J
202 CONTINUE
IF(BX-0.00001)320,320,300

```

```

C      COMPUTE ROTATION
300    BX=X(LA, LB)*X(LA, LB)
      D=X(LA, LA)-X(LB, LB)
      R=SQRT(D*D+4.*BX)
      A=SQRT(ABS((R+D)/(2.0*R)))
      IF(0.707-A)302,302,301
301    B=0.0-A
      A=SQRT(1.0-B*B)
      GO TO 303
302    B=-SQRT(1.0-A*A)
303    IF(D/X(LA, LB))304,310,310
304    B=0.0-B
C      ORTHOGONAL ROTATION OF MATRIX
310    DO 313 J=1,NDIM
      IF(LA-J)311,313,311
311    IF(LB-J)312,313,312
312    X(LA, J)=A*X(J, LA)-B*X(J, LB)
313    CONTINUE
      DO 314 J=1,NDIM
      X(J, LA)=X(LA, J)
314    X(J, LB)=X(LB, J)
      D=X(LA, LA)+X(LB, LB)
      X(LA, LA)=A*A*X(LA, LA)+B*B*X(LB, LB)-2.*A*B*X(LA, LB)
      X(LB, LB)=D-X(LA, LA)
      X(LA, LB)=0.0
      X(LB, LA)=0.0
C      ENTER ROTATION MATRIX
      DO 315 J=1,NDIM
      BX=E(J, LA)
      E(J, LA)=A*BX-B*E(J, LB)
315    E(J, LB)=B*BX+A*E(J, LB)
      GO TO 200
C      TEST DIAGONALIZED MATRIX
320    BX=0.00004
      JA=NDIM-1
      DO 323 I=1,JA
      JB=I+1
      DO 323 J=JB,NDIM
      IF(X(I, J))321,323,321
321    R=ABS(X(I, J)/(X(I, I)-X(J, J)))
      IF(R-BX)323,323,322
322    BX=R
      LA=I
      LB=J
323    CONTINUE
      IF(BX-0.00005)450,450,300
C      CALC TRANSITION INTENSITIES AND FREQUENCIES
450    DO 451 I=1,NDIM
451    H(I)=X(I, I)
      PRINT 169
169    FORMAT(5X, *ENERGY LEVELS*)

```

```

PRINT 1008,(H(I),I=1,36)
1000  FORMAT(/3H G=,F11.5,4H RD=,F14.1,4H RE=,F10.5,
      4H AZ=F10.5,4H AX=,F
110.5,4H AY=,F10.5,7H HDPPH=,F8.2//)
1008  FORMAT(2X,6F10.2)
      DO 65 I=1,30
65    HH(I)=H(I)-H(I+6)
500   FORMAT(2X,10H CALCULATED,3X,12H EXPERIMENTAL)
50    FORMAT(2X,F8.2,5X,F8.2)
      GZ=HDPPH*HNOT/G
2000  FORMAT(7H GX AXIS)
      N1=1
      DO 5020 IJ=1,3
      N2=N1+9
5000  PRINT 5000,(I,I=N1,N2)
      FORMAT(/25X,10I10/)
      PRINT 5001,(Y(I),I=N1,N2)
      PRINT 5002,(HH(I),I=N1,N2)
5001  FORMAT(5X,*OBSERVED*,12X,10F10.2)
5002  FORMAT(5X,*CALCULATED*,10X,10F10.2)
5020  N1=N1+10
2001  FORMAT(5X,8E12.5)
      PRINT 2001,G,GZ,HNOT,RD,RE,AZ,AX,AY
      DO 324 I=1,30
      DEF(I)=Y(I)-HH(I)
324   DEFS(I)=DEF(I)**2
      DSUM=0.0
      DO 325 I=1,30
325   DSUM=DSUM+DEFS(I)
      DAVE=DSUM/30.0
      DELA=SQRTF(DAVE)
      PRINT 76
76    FORMAT(5X,*STANDARD DEVIATION FOR THE THIRTY LINE
      SPECTRUM*)
      PRINT 100,DELA
      HH(37)=HH(1)-HH(6)
      HH(38)=HH(7)-HH(12)
      HH(39)=HH(13)-HH(18)
      HH(40)=HH(19)-HH(24)
      HH(41)=HH(25)-HH(30)
      H(37)=Y(1)-Y(6)
      H(38)=Y(7)-Y(12)
      H(39)=Y(13)-Y(18)
      H(40)=Y(19)-Y(24)
      H(41)=Y(25)-Y(30)
      PRINT 70
70    FORMAT(30H SEPARATION FOR EACH TRANSITION)
      PRINT 500
      PRINT 50,(HH(I),H(I),I=37,41)
      DO 69 I=1,36
69    HF(I)=H(I)-HF(I)

```

```

DO 68 I=1,5
J=6*I
K=J-5
JEP=J+6
KEP=J+1
68 HFC(I)=-((Y(J)-Y(K)+HF(K)+HF(JEP)-HF(J)-HF(KEP))/5.
PRINT 99,(HFC(I),I=1,5)
99 FORMAT(1X,5F8.2)
SUM=0.
DO 700 I=1,5
700 SUM=SUM+HFC(I)
120 AVE=SUM/5.0
PRINT 75
75 FORMAT(18HHYPERFINE CONSTANT)
PRINT 100, AVE
100 FORMAT(5X,F8.2)
DO 71 I=6,10
J=I-5
71 HFC(I)=(AVE-HFC(J))*2
ASUM=0.
DO 72 I=6,10
72 ASUM=ASUM+HFC(I)
DELS=ASUM/5.
DEL=SQRTF(DELS)
PRINT 73
73 FORMAT(18HSTANDARD DEVIATION)
PRINT 100, DEL
PRINT 444, BFZ, BFT, BFF
444 FORMAT(1X,3E12.5)
RD=RD-1.
555 CONTINUE
STOP
END
$ENTRY

```

After this the data cards are placed.  
 The eigenvectors can be asked to be printed in case they are needed as in determining the orientation of magnetic susceptibility axes with respect to the crystallographic axes in the case of vanadyl-doped caesium sulphate

Experimental observations confirmed this to within 1°.

Temperature variation studies from 300 °K to 77 °K show that there is no abrupt change in the spectral patterns. The spectrum recorded at 77 °K with a small crystal in the low temperature tube is shown in Fig.(3.6). Within the temperature range of 77 °K to room temperature, ( $\sim 297$  °K), the overall spread of the spectrum gradually increases as we go from low temperature to high temperature. Fig.(3.7) shows the temperature variation of the parameters D and E within this range. It is seen that the change in  $E^*$  is about 4% while in  $D^*$  the change is 14%. This alters the ratio of  $D^*$  to  $E^*$  giving probably an indication of the overlap and covalency effects as suggested by Watkins<sup>16</sup>. The smooth variation of the parameters D and E suggests that structural changes involving first or second order phase transitions have probably not occurred in this temperature range. Such changes are expected in  $\text{Cs}_2\text{SO}_4$  doped with  $\text{Mn}^{2+}$  as this crystal is isomorphous with  $\text{K}_2\text{SO}_4$  where a second order phase transition is indicated.<sup>3</sup>

The line widths at 77 °K for  $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition are found to be the same as those of  $\pm 5/2 \leftrightarrow \pm 3/2$  transitions ( $\sim 9$  oersted) indicating the crystals grown from slow evaporation of saturated solution do not develop

TABLE 3.7

The lines of  $\text{Mn}^{2+}:\text{Cs}_2\text{SO}_4$  at 77 °KH || x-axis of the complex  
(ALL VALUES IN OERSTED)

DPPH <sup>a</sup>	3316																			
Line	-3/2	Ob- serv- ed	-5/2	cal- culat- ed	-1/2	Ob- serv- ed	-3/2	cal- culat- ed	-1/2	Ob- serv- ed	+1/2	cal- culat- ed	+3/2	Ob- serv- ed	+1/2	Cal- culat- ed	+5/2	Ob- serv- ed	+3/2	cal- culat- ed
1939			1928		2192		2181		2656		2645		3288		3296		4739		4745	
2024			2011		2274		2267		2745		2733		3397		3387		4822		4838	
2107			2096		2368		2355		2838		2823		3487		3480		4913		4934	
2192			2184		2459		2445		2932		2916		3585		3575		5012		5032	
2283			2275		2552		2538		3027		3012		3672		3673		5116		5133	
2380			2368		2645		2634		3125		3110		3756		3774		5229		5236	

Standard deviation 13 <sup>a</sup>Diphenylpicrylhydrazyl

Input data (for second order perturbation equations 3.2(a)):

 $A_x = -93$  ;  $A_z = -93$  ;  $A_y = -93$  ;  $H_{0x} = 3304$  ( $g_x = 2.0109$ ) $D = 401$  ;  $E_x = 470$  ; $(b_4^0)_x = -20$  ;  $(b_4^2)_x = 56$

(I of  $V^{51} = 7/2$ ) the EPR spectrum shows a characteristic eight line hyperfine structure. The EPR spectrum of  $VO^{2+}$  when having an orthorhombic site symmetry can be described in a principal axis system by a spin-Hamiltonian type<sup>10</sup> :

$$\underline{H} = \beta(g_z H_z S_z + g_x H_x S_x + g_y H_y S_y) \\ + A I_z S_z + B I_x S_x + C I_y S_y$$

a solution of which gives the magnetic field resonance values by<sup>11</sup>

$$H = H_0 - Km - \frac{1}{2H_0} [a(15/4 - m^2) + bm^2 + cm] \quad \dots \quad (4.1)$$

where

$$\begin{aligned} K^2 g^2 &= A^2 g_z^2 \cos^2 \theta + D^2 g^2 \sin^2 \theta \\ A^2 - D^2 &= E \\ D^2 g_{\perp}^2 &= B^2 g_x^2 \cos^2 \delta + C^2 g_y^2 \sin^2 \delta \\ B^2 - C^2 &= F \\ a &= [A^2 D^4 + B^2 C^2 K^2 - A^2 E^2 (\xi g_x g_y g_z / g g_{\perp}^2)^2] / 2 D^2 K^2 \\ b &= [F^2 (g_{\perp} g_z \cos \theta \sin \theta / g^2)^2 + E^2 (\eta g_x g_y / g_{\perp}^2)^2] / K^2 \\ c &= E^2 (\eta g_x g_y / g^2)^2 / D^2 \\ \xi &= \cos \delta \sin \delta \cos \theta \\ \eta &= \cos \delta \sin \delta \sin \theta \end{aligned}$$

$\theta$  and  $\delta$  being polar angles of the direction of the



is found to show the largest hyperfine structure spread, (lines marked a in Fig.(4.2), when H is along the c-axis of the crystal suggesting that the z-axis of the complex is along the c axis. It was also found that this spectrum has minimum hyperfine structure spread when H is along a-direction, (see lines marked b in Fig.(4.3) and those marked c in Fig.(4.4) respectively. This observation suggests that the x and y axes of the complex I are along the crystallographic b and c axes. The spectrum of complex II has been found to have a maximum spread when the magnetic field direction H makes an angle of  $30^\circ$  with c-axis in the bc-plane, (see lines marked d in Fig.4.5), and a minimum spread, (see lines marked e in Fig.4.6), at an angle of  $90^\circ$  in the same plane from the direction of maximum spread. These directions of maximum and minimum spectral spreads are very likely the z and x directions. The spectral lines corresponding to H || y axis of complex II are shown in Fig.(4.3) and are marked f. The y axis of this complex coincides with the crystallographic a-axis.

The angular variation of the spectrum corresponding to complex III has indicated that the maximum hyperfine structure spread of the spectrum comes up when H is nearly (but not exactly) parallel to the crystalline a-axis. After studying the angular variation of the EPR spectrum of this complex in the three crystallographic planes, the principal values of the g and A tensors

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at the alkali site associated with a second neighbour alkali vacancy while that responsible for the spectrum  $\text{III}_4$  is again a similar  $\text{Mn}^{2+}$  ion but associated probably with a fourth neighbour alkali vacancy. Both the complexes have their site symmetry axes along the  $\langle 100 \rangle$  direction. It has been observed that spectrum II is more intense than spectrum  $\text{III}_4$  which is again more intense than spectrum  $\text{III}_2$ . This observation indicates clearly that in  $\text{Mn}^{2+}:\text{NaF}$ , remote charge compensation is preferred to the local charge compensation.<sup>†</sup>

All the spectra II,  $\text{III}_2$  and  $\text{III}_4$  show superhyperfine structure. The spectra have been analysed using the expressions indicated earlier and the constants obtained are given in Table 5.4 where the data available from the earlier work are also included. The spectrum II is overlapped by the transition  $M=\frac{1}{2} \leftrightarrow -\frac{1}{2}$  of the spectrum  $\text{III}_4$  and also by that of the spectrum  $\text{III}_2$ . Its separate existence has been confirmed by taking the spectrum of a powdered sample as has been done by Veigele and Tani<sup>14</sup> in the case of  $\text{Mn}^{2+}:\text{KF}$ . Figure 5.1 shows the spectrum II as obtained from such a powdered or polycrystalline sample showing clearly the six hyperfine lines along with the superhyperfine structure.

<sup>†</sup> It may be mentioned that Hall et al<sup>13</sup> state that  $\text{Mn}^{2+}$  ions unassociated with vacancies, that is, at cubic sites, are not present at room temperature. The cubic spectrum is observed only beyond 300 °C, which rapidly revert to the preheated condition after cooling.

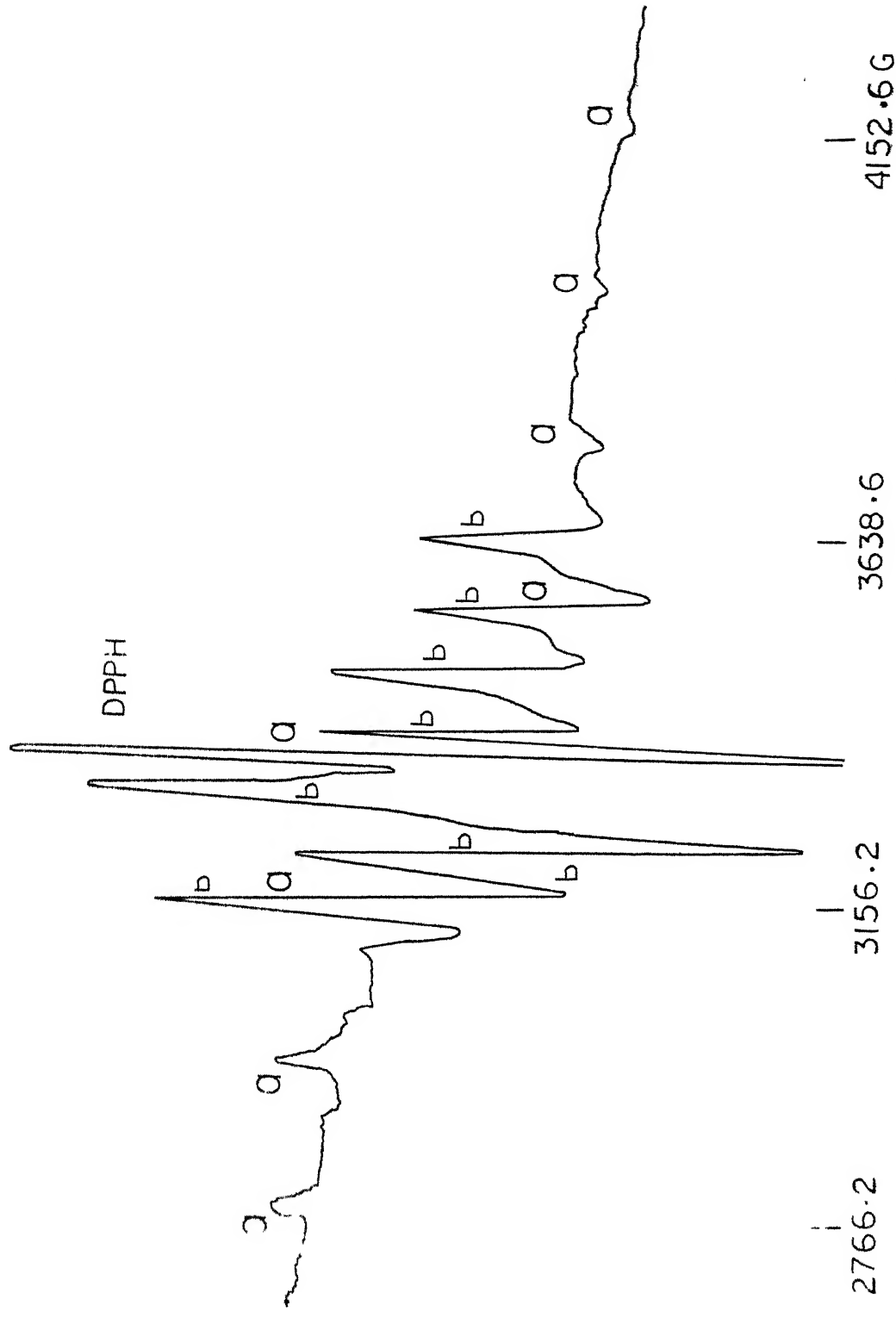


FIG.6.2 SPECTRUM II ELECTRON PARAMAGNETIC RESONANCE OF  $\text{VO}^{2+}$  IN  $\text{NaCl}$  AT LIQUID NITROGEN TEMPERATURE. LINES MARKED a ARE PARALLEL TRANSITIONS AND THOSE MARKED b ARE PERPENDICULAR TRANSITIONS. THE X-COORDINATE REPRESENTS MAGNETIC FIELD VALUES IN GAUSS.

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APPENDIX B1

Computer programme used to find the spin-Hamiltonian parameters for  $Mn^{++}:Cs_2SO_4$  system using equations 3.2

$H(I)$  are the fine structure fields in gauss or oersted. FNOT, RD, RE, BFT are respectively  $H_0$ ,  $D$ ,  $E$ ,  $b_4^0$  and  $b_4^2$

PPH is the DPPH field marker value while PH is the g-value of DPPH.

The program can be used to iterate for any number of times NUM. A least-square fit with the calculated field values HC(I) is incorporated.

```

C C PHROO6 AVJ
  DIMENSION H(5), HC(5), DIF(5)
  READ 1234, NUM
1234 FORMAT(I3)
  DO 555 IND=1, NUM
  READ 1, (H(I), I=1, 5)
  1  FORMAT(1X, 5F7.1)
  READ 1, FNOT, RD, RE, BFZ, BFT
  READ 4, PPH, PH
  2  FORMAT(1X, 5E12.5)
  3  FORMAT(1X, 3F7.1)
  4  FORMAT(1X, 2E12.5)
  PRINT 1234, IND
  PRINT 1, (H(I), I=1, 5)
  PRINT 1, FNOT, RD, RE, BFZ, BFT
  PRINT 4, PPH, PH
  SE=RE**2
  HC(1)=FNOT-4.*RD+9.*SE/(H(1)+RD)-5.*SE/(H(1)+3.*RD)
    -4.*BFZ
  HC(2)=FNOT-9.*SE/(H(2)+RD)+9.*SE/(H(2)-RD)-5.*SE/(H(2)
    +3.*RD)+5.0*
  1BFZ-2.*RD
  HC(3)=FNOT-9.*SE/(H(3)-RD)+5.*SE/(H(3)+3.*RD)+5.*SE/(H
    (3)-3.*RD)-9
  1.*SE/(H(3)+RD)
  HC(4)=FNOT+2.*RD+9.*SE/(H(4)+RD)-9.*SE/(H(4)-RD)-5.*
    SE/(H(4)-3.*RD
  1)-5.0*BFZ
  HC(5)=FNOT+4.*RD+9.*SE/(H(5)-RD)-5.*SE/H(5)-3.*RD)+
    4.*BFZ
  TEMP=1.5*RE*BFT/FNOT
  HC(1)=HC(1)+TEMP+TEMP
  HC(5)=HC(5)+TEMP+TEMP
  HC(2)=HC(2)+TEMP
  HC(4)=HC(4)+TEMP
  HC(3)=HC(3)-TEMP-TEMP-TEMP-TEMP
  DO 11 I=1, 5
  11 DIF(I)=(H(I)-HC(I))**2
  SUM=0.

```